Photosensitive Ionic Nematic Liquid Crystalline Complexes Based on Dendrimers and Hyperbranched Polymers and a Cyanoazobenzene Carboxylic Acid†

Mercedes Marcos,*,‡ Rafael Alcalá,§ Joaquín Barberá,‡ Pilar Romero,‡ Carlos Sánchez,*,§ and José Luis Serrano‡

Química Orgánica and Física de la Materia Condensada, Facultad de Ciencias-Instituto de Ciencia de Materiales de Aragón (ICMA), Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas (CSIC), 50009 Zaragoza, Spain

Received February 6, 2008. Revised Manuscript Received April 30, 2008. Accepted May 27, 2008

The synthesis and characterization of ionic liquid crystal dendrimers and hyperbranched polymers based on the ammonium salts of commercially available dendrimers poly(propylene imine) [PPI-$(NH_2)_n$] (with $n = 16$), and poly(amidoamine) [PAMAM-$(NH_2)_n$] (with $n = 16$), and random hyperbranched poly(ethyleneimine) (PEI) and the prepared fully methylated PEI (namely PEIMe) with 5-(4-cyanophenylazophenyloxy)pentanoic acid (CAzPA) are reported. The occurrence of proton transfer from the carboxylic acid to the amine groups was confirmed by IR and NMR measurements. 5-(4-Cyanophenylazophenyloxy)pentanoic acid does not show mesogenic properties. However, all synthesized ionic complexes displayed a nematic mesophase. The liquid crystalline behavior was investigated by means of differential scanning calorimetry, polarizing light optical microscopy, and X-ray diffractometry. Themogravimetry analysis was carried out in order to determine the stability of the complexes, all of which have their mesophase−isotropic liquid transition under the temperature of 5% weight loss. Birefringence has been induced using 488 nm linearly polarized light in thin films of the ionic dendritic polymers containing azobenzene moieties. High and stable values of the in-plane order parameter up to 0.67 have been reached.

Introduction

Dendrimers and hyperbranched polymers have attracted significant interest because of their unique architecture and novel properties, which distinguish them from their linear analogues. Such properties include good solubility, special viscosity behavior, and high density of their functional groups.[1]

Dendrimers are multivalent, well-defined, and highly branched macromolecules that tend to adopt a globular shape in solution. The stepwise synthesis of dendrimers allows for a large degree of control over the molecular architecture and the design of dendrimers with different morphologies and properties. Unfortunately, preparation of dendrimers takes a long time for the isolation and purification procedures. For that reason, hyperbranched polymers prepared in one-step self-polymerization of AB_x-type multifunctional monomers have gained increasing interest.[2]

Most of the liquid crystal dendrimers reported up to date are constituted by covalent neutral molecules.[3,4] However, some examples of ionic thermotropic LC dendritic polymers have also been recently described.[5–23] As can be easily understood, amphiphilic microsegregation acts as a driving

† Dedicated to the memory of Naomi Hoshino-Miyajima (Hokkaido University, Japan).

* To whom correspondence should be addressed. E-mail: mmarcos@unizar.es (M.M.); carloss@unizar.es (C.S.)

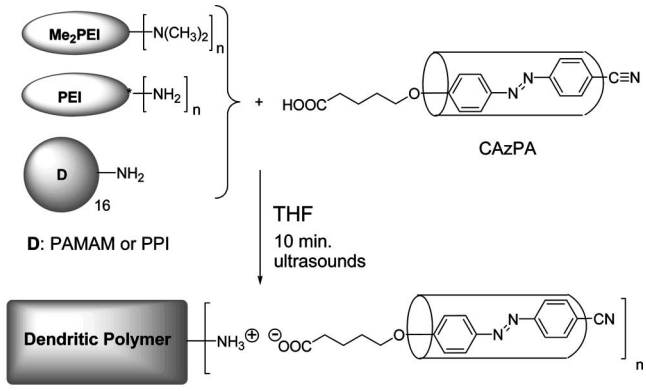
‡ Química Orgánica.

§ Física de la Materia Condensada.

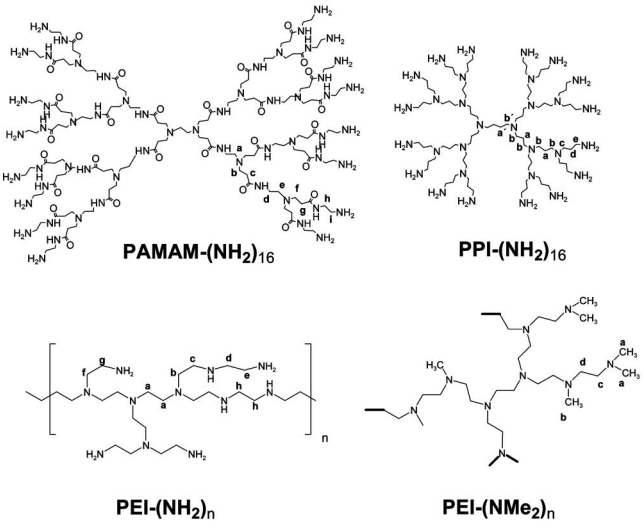
(1) Fréchet, J. M.; Tomalia, D. A. *Dendrimers and Other Dendritic Polymers*; Wiley Series on Polymer Science; John Wiley and Sons, Ltd.: New York, 2001.
(2) Gao, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29*, 183.
(3) Donnio, B.; Guillon, D. *Adv. Polym. Sci.* **2006**, *201*, 45.
(4) Marcos, M.; Martín-Rapún, R.; Omenat, A.; Serrano, J. L. *Chem. Soc. Rev.* **2007**, *36*, 1889.
(5) Faul, Ch. F.J.; Antonietti, M. *Adv. Mater.* **2003**, *15*, 673.
(6) Binnemans, K. *Chem. Rev.* **2005**, *105*, 4148.
(7) Martín-Rapún, R.; Marcos, M.; Omenat, A.; Barberá, J.; Romero, P.; Serrano, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 7397.
(8) Ujiie, S.; Takagi, S.; Sato, M. *High Perform. Polym.* **1998**, *10*, 139.
(9) Thünemann, A. F.; General, S. *Langmuir* **2000**, *16*, 9634.
(10) Zhu, S.; Shi, H.; Zhao, Y.; Jiang, S.; Lu, Y.; Cai, Y.; Wang, D.; Han, Ch. C.; Xu, D. *Macromol. Rapid. Commun.* **2005**, *26*, 226.
(11) Friberg, S. E.; Podzimek, M.; Tomalia, D. A.; Hedstrand, D. M. *Mol. Cryst. Liq. Cryst.* **1988**, *164*, 157.
(12) Ujiie, S.; Yano, Y.; Mori, A. *Mol. Cryst. Liq. Cryst.* **2004**, *411*, 483.
(13) Faul, C. F. J.; Antonietti, M.; Hentze, H. P.; Smarsly, B. *Colloids Surf., A* **2003**, *212*, 115.
(14) Takahashi, T.; Kimura, T.; Sakurai, K. *Polymer* **1999**, *40*, 5939.
(15) Ujiie, S.; Osaka, M.; Yano, Y.; Iimura, K. *Kobunshi Ronbunshu* **2000**, *57*, 797.
(16) Tsiourvas, D.; Felekis, T.; Sideratou, Z.; Paleos, C. M. *Liq. Cryst.* **2004**, *31*, 739.
(17) Cook, A. G.; Baumeinster, U.; Tschierske, C. *J. Mater. Chem.* **2005**, *15*, 1708.
(18) Chen, Y.; Shen, Z.; Gehringer, L.; Frey, H.; Stiriba, S-E. *Macromol. Rapid Commun.* **2006**, *27*, 69.
(19) Van de Coevering, R.; Bruijnincx, P. C. A.; van Walree, C. A.; Klein Gebbink, R. J. M.; Van Koten, G. *Eur. J. Org. Chem.* **2007**, 2931.
(20) Marcos, M.; Martín-Rapún, R.; Omenat, A.; Barberá, J.; Serrano, J. L. *Chem. Mater.* **2006**, *18*, 1206.
(21) Martín-Rapún, R.; Marcos, M.; Omenat, A.; Serrano, J. L.; Taffin de Givenchy, E.; Guittard, F. *Liq. Cryst.* **2007**, *34*, 395.
(22) Fitié, C. F. C.; Tomatsu, I.; Byelov, D.; de Jeu, W. H.; Sijbesma, R. P. *Chem. Mater.* **2008**, *20*, 2394.
(23) Noguchi, T.; Kishikawa, K.; Kohmoto, S. *Chem. Lett.* **2008**, *37*, 12.

10.1021/cm800382y CCC: $40.75
Published on Web 07/29/2008

Scheme 1. (a) Synthetic Route for Ionic Mesogenic Complexes and (b) Structure of Dendrimers and Random Hyperbranched Polymers Used



(a)



(b)

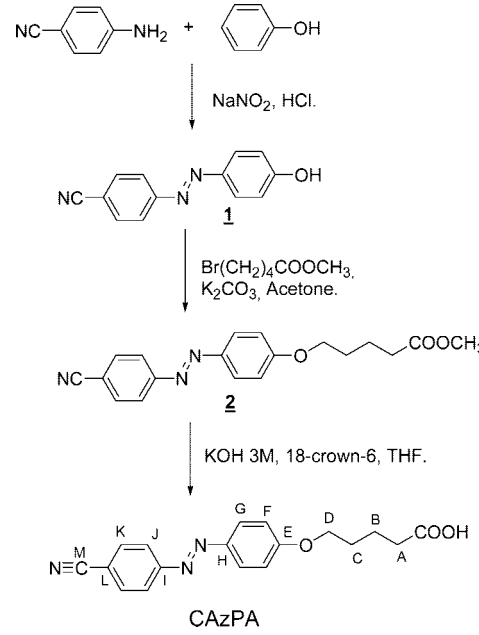
force capable of organizing these supermolecules within ordered structures giving rise to mesomorphic behavior.

In previous work,[7,20,21] we studied several families of ionic homodendrimers which are formed by spontaneous assembly of long-chain carboxylic acids or (mono, di, or tri)alkoxybenzoic acids onto the surface of amino-terminated poly(propylene imine) (PPI-$(NH_2)_n$) and poly(amidoamine) (PAMAM-$(NH_2)_n$) (n = 4, 8, 16, 32, 64) which show lamellar mesomorphism, namely, smectic A. The exception to this tendency is found for PPI-derived dendrimers of the fifth generation, which self-assemble into a columnar supramolecular structure. Also, dendrimers containing tridecyloxybenzoic acids exhibit columnar mesomorphism, rectangular or hexagonal, depending on the generation number.

Although most of the ionic liquid crystal complexes described are made up of units derived from aliphatic carboxylic acids, some examples of ionic liquid crystals made up of units derived from carboxylic acids containing rodlike core units, which can be already liquid crystalline by themselves or not, have been reported.

Ujiie et al.[15] reported in 2000 the appearance of smectic A liquid crystal properties in ionic complexes derived from

Scheme 2. Synthetic Route of 5-(*p*-Cyanophenylazophenyloxy)pentanoic Acid (CAzPA)



branched PEI, poly(allylamine) (PAA), and PAMAM and an azoderivative carboxylic acid.

Tsiourvas et al.[16] described in 2004 the thermotropic liquid crystalline behavior of a family of ionic dendrimers derived from the protonation of poly(propylene imine) (PPI) with a cholesterol-based carboxylic acid. These LC dendrimers show smectic C* and smectic A mesophases.

In 2005, Tschierske et al.[17] reported the preparation of ionic complexes of facial amphiphilic carboxylic acids, which contain a π-terphenyl core, with PPI dendrimer of first to fifth generations referred to as "dendroelectrolyte amphiphilic complexes". They observed a smectic A mesophase, two different square columnar phases, a hexagonal organization of columns, and two additional columnar phases with unknown structures depending on the generation, the length of the flexible spacer, or the ratio of dendrimer to carboxylic acid.

In 2006, Frey et al.[18] reported for the first time obtaining a nematic mesophase with ionic dendritic polymers prepared from the noncovalent interaction of methylated hyperbranched (PEIMe)s with a mesogen-based carboxylic acid, namely 5-(p-cyanobiphenoxy)pentanoic.

At the same time, Faul et al.[24] reported for the first time the photoalignment of photosensitive ISA (ionic self-assembly) complexes of low molecular weight consisting of charged azobenzene-containing photosensitive units complexed with oppositely charged surfactants, and they demonstrated that the irradiation of films of these complexes with linearly polarized light leads to very effective induction of optical anisotropy showing thermal and long-term stability.

Taking all this into account together with our experience in the study of liquid crystalline dendrimers[4,7,20,21] and photoinduced effects in covalent azo functionalizated den-

(24) Zakrevsky, Y.; Stumpe, J.; Faul, C. J. *Adv. Mater.* **2006**, *18*, 2133.

Table 1. ^{1}H NMR Data for the 5-(4-Cyanophenylazophenyloxy)pentanoic Acid, Dendritic Polymers and Their Complexes: PAMAM-CAzPA, PPI-CAzPA, PEI-CAzPA, PEIMe-CAzPA

compd	COOH	$\underline{CH_2}COO$	$\underline{CH_2}CH_2COO$	$\underline{NH}CO$	$-\underline{CH_2}NH_3^+$ $-\underline{CH_2}NH_2$	$-\underline{CH_2}CH_2NH_3^+$ $-\underline{CH_2}CH_2NH_2$
CAzPA	11.80	2.30	1.67			
PAMAM-NH_2				7.74	2.59	3.07
PAMAM-CAzPA		2.27	1.71	7.76,7.67	2.61	3.09
PPI-NH_2					2.55	1.44
PPI-CAzPA		2.25	1.69		2.60	1.49
PEI-NH_2					2.57/2.59	2.41/2.51
PEI-CAzPA		2.25	1.69		2.67/2.67	2.48/2.58
PEIMe[a]					2.4−2.6	2.4−2.6
PEIMe-CAzPA[b]		2.29	1.69		2.41−2.31	2.5

[a] PEIMe: $N(\underline{CH_3})_2$ 2.22, $N-\underline{CH_3}$ 2.25. [b] PEIMe-CAzPA; $N(\underline{CH_3})_2$ 2.15, $N-\underline{CH_3}$ 2.18.

Table 2. ^{13}C NMR Data for the 5-(4-Cyanophenylazophenyloxy)pentanoic Acid, Dendritic Polymers, and Their Complexes: PAMAM-CAzPA, PPI-CAzPA, PEI-CAzPA, PEIMe-CAzPA

compd	$\underline{COOH}/\underline{COO}^-$	$\underline{CH_2}COO$	$\underline{CH_2}CH_2COO$	$NH\underline{CO}$	$\underline{CH_2}$ NH_3^+ $\underline{CH_2}NH_2$	$\underline{CH_2}CH_2NH_3^+$ $\underline{CH_2}CH_2NH_2$
CAzPA	173.8	33.1	20.9			
PAMAM-NH_2				171.8−171.6	41.2	42.1
PAMAM-CAzPA	175.1	34.1	21.1	171.3−171.0	40.7	41.4
PPI-NH_2					39.9	30.9
PPI-CAzPA	174.1	33.8	21.1		39.1	29.6
PEI-NH_2					39.7/41.4	57.9/52.4
PEI-CAzPA	175.0	34.7	21.1		38.4/40.2	55.3/50.2
PEIMe[a]					54.2−57.0	51.6−53.1
PEIMe-CAzPA[b]	175.0	33.1	21.0		54.0−57.0	51.5−53.6

[a] PEIMe: $N(\underline{CH_3})_2$ 44.9, $N-\underline{CH_3}$ 42.2. [b] PEIMe-CAzPA: $N(\underline{CH_3})_2$ 45.3, $N-\underline{CH_3}$ 42.5.

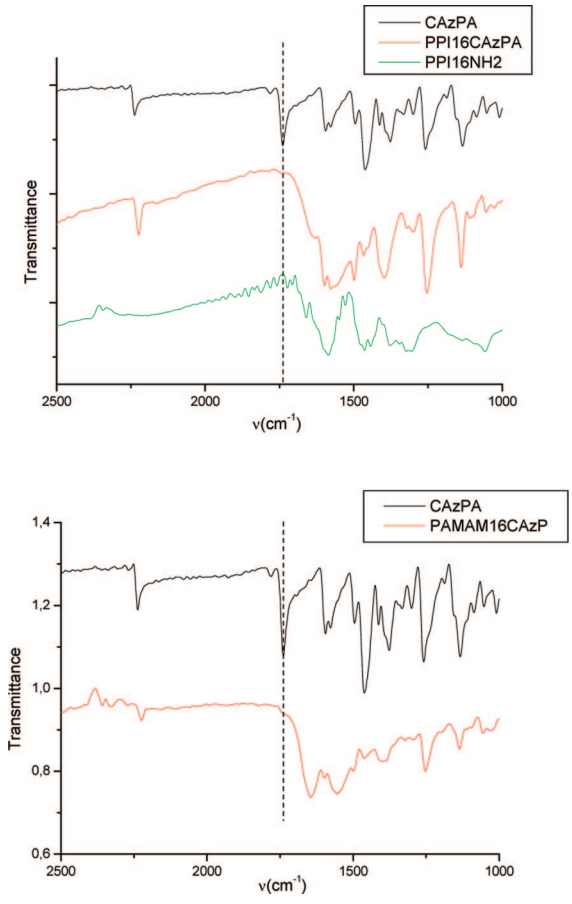


Figure 1. FTIR spectra of complexes PPI-CAzPA and PAMAM-CAzPA compared with that of the CAzPA acid.

drimers,[25] we have undertaken an investigation on the synthesis and characterization of ionic liquid crystal dendrimers and hyperbranched polymers complexed with an azobenzene moeity, in the hope of obtaining ionic photosensitive nematic materials.

Thus, in the current paper we report the design, synthesis, characterization, and mesophase behavior of ionic LC complexes by self-assembly of two commercially available dendrimers: poly(propylene imine) PPI-$(NH_2)_{16}$ ($G = 3$) and poly(amidoamine) PAMAM-$(NH_2)_{16}$ ($G = 2$) with 16 terminal branches and the random hyperbranched poly(ethyleneimine) (PEI) polymer and fully methylated PEIMe with an aromatic-based carboxylic acid: 5-(4-cyanophenylazophenyloxy)pentanoic acid (CAzPA) (see Scheme 1), as well as the photoinduced response of these ionic complexes containing azo groups.

Experimental Section

Materials and General Techniques. All chemical reagents were purchased from Aldrich and used as received. Hyperbranched poly(ethyleneimine) ($M_{n\text{-}1} \times 10^{-4}$ g/mol, $M_w/M_n = 2.5$, NH_2:NH:N = 33:40:27) was purchased from Aldrich. PPI-$(NH_2)_{16}$ dendrimer ($G = 3$) was purchased from SyMO-Chem BV (Eindhoven, the Netherlands). Starburst-PAMAM-$(NH_2)_{16}$ dendrimer ($G = 2$) was obtained from Dendritech, Inc. All of them were used as received. Dialysis tubing, benzoylated useful for separating compounds with a molecular weight of δ 1200 from compounds with a molecular weight >2000 was purchased from Sigma.

The infrared spectra of all the complexes were obtained with a Mattson Genesis II FTIR spectrophotometer in the 400−4000 cm^{-1} spectral range using KBr pellets. All nuclear magnetic resonance (NMR) experiments (^{1}H, ^{13}C, ^{1}H−^{1}H COSY, and ^{1}H−^{13}C HSQC) were recorded using standard pulse sequences on a Bruker AVANCE 500 spectrometer operating at 500.13 MHz for ^{1}H and 125.7 MHz for ^{13}C and on a Bruker AVANCE 400 spectrometer operating at 400.13 MHz for ^{1}H and 100.5 MHz for ^{13}C. The spectra were measured in DMSO-d_6 solutions at 333 K. Chemical shifts are given in ppm relative to TMS, and the solvent residual peak was used as internal standard.

(25) Alcalá, R.; Giménez, R.; Oriol, L.; Piñol, M.; Serrano, J. L.; Villacampa, B.; Viñuales, A. I. *Chem. Mater.* **2007**, *19*, 235.

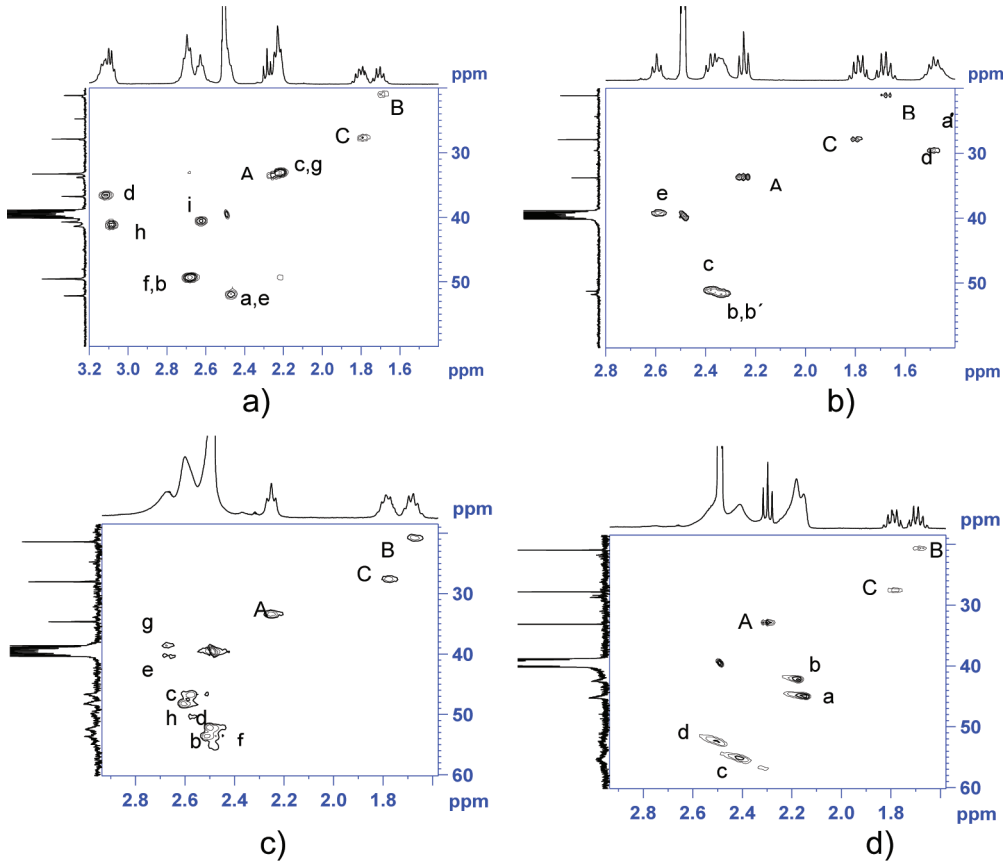


Figure 2. Two-dimensional correlated $^{1}H-^{13}C$ HSQC experiments in the interval from 1 to 3 ppm of the complexes (a) PAMAM-CAzPA, (b) PPI-CAzPA, (c) PEI-CAzPA, and (d) PEIMe-CAzPA.

The optical textures of the mesophases were studied with a Olympus BH-2 polarizing microscope equipped with a Linkan THMS hot stage, a central processor, and a CS196 cooling system. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a DSC 2910 from TA Instruments operated at a scanning rate of 10 °C min^{-1} on both heating and cooling cycles. The apparatus was calibrated with indium (156.6 °C, 28.4 J g^{-1}) as the standard. The temperatures were read at the maximum of the transition peaks, and the glass transition temperature was read at the midpoint of the heat capacity increase. Thermogravimetric analysis (TGA) was performed using a TA instrument STD 2960 simultaneous TGA-DTA at a rate of 10 °C min^{-1} under argon atmosphere. TGA data are given as the onset of the descomposition curve. The XRD patterns were obtained with a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu Kα beam. The sample was held in Lindemann glass capillaries (1 mm diameter) and heated, when necessary, with a variable-temperature oven. The capillary axis is perpendicular to the X-ray beam, and the pattern is collected on flat photographic film perpendicular to the X-ray beam. Spacings were obtained via Bragg's law.

Films and Optical Studies. Materials were first dissolved in cyclohexanone (PPI-CAzPA, PEI-CAzPA, and PEIMe-CAzPA) and methanol (PAMAM-CAzPA) by using a magnetic stirrer. Cyclohexanone and methanol were heated up to 60 and 40 °C, respectively, to assist the solution of the materials and kept at these temperatures to avoid precipitation until film formation. The films are prepared by spin coating (600 rpm, 600 rpm/s, 240 s) onto clean fused silica substrates. Films were dried overnight in a vacuum oven at 60 °C. Film thicknesses were measured using a DEKTAK profilometer obtaining values in the thickness range 200−300 nm. Before optical experiments in the films, a thermal annealing was performed by heating the samples up to 100 °C for 10 min and cooling down again to room temperature by putting them on a metallic plate. A Varian Cary 500 UV−vis−IR spectrophotometer was used for optical absorption and dichroism measurements. For these last measurements, a linear polarizer was introduced in front of the film. Birefringence (Δn) measurements were performed using a standard setup reported elsewhere.[26] The sample was placed between crossed polarizers with their polarization directions at ±45° with the vertical axis and irradiated with vertically polarized 488 nm light from an Ar^{+} laser. The light from a 780 nm diode laser (10 mW) transmitted through the polarizer−sample−polarizer system was measured with a Si photodetector. It has been checked that the 780 nm light does not introduce any changes in the optical properties of the film. The transmitted intensity I is given by the following equation:

$$I = I_0 \sin^2(\pi|\Delta n|d/\lambda)$$

where I_0 is the intensity transmitted by the "as-quenched" films between parallel polarizers, d is the film thickness, and λ is the wavelength of the measuring light (780 nm).

Nomenclature. 5-(4-Cyanophenylazophenyloxy)pentanoic acid is designed as CAzPA. Ionic functionalized dendrimers derived from poly(amidoamine) with 16 terminal NH_2 groups and poly(propylene imine) with 16 terminal NH_2 groups are denoted by PAMAM-CAzPA and PPI-CAzPA, respectively. Ionic random hyperbranched polymers derived from poly(ethylenimine) and fully methylated polyethylenimine are denoted by PEI-CAzPA and PEIMe-CAzPA, respectively.

(26) Sánchez, C.; Alcalá, R.; Hvilsted, S.; Ramanujam, P. S. *J. Appl. Phys.* **2003**, *93*, 4454.

Synthesis. The synthesis of 5-(4-cyanophenylazophenyloxy)pentanoic acid (CAzPA) was carried out as shown in Scheme 2.

The synthetic procedures and characterization data (IR and NMR) for the acid and the intermediates are gathered in the Supporting Information.

Typical Procedure for the Synthesis of the Ionic Dendritic-Functionalized Polymers. The ionic complexes were prepared following Scheme 1 by addition (approx 100 mg) of amine-termined PAMAM-$(NH_2)_{16}$, PPI-$(NH_2)_{16}$ dendrimers or random hyperbranched PEI-$(NH_2)_n$ polymer, and their methylated derivative (prepared following the method described by Frey et al.[18]), dissolved in dry tetrahydrofuran (THF) to a solution of THF containing the acid in an approximately 1:1 stoichiometry between the acid and each of the N-terminal amine groups present in the dendrimers and hyperbranched polymers following the method previously described.[7] The mixture underwent ultrasonication for 10 min, and then it was slowly evaporated at room temperature and dried in vacuum at 40 °C until the weight remained constant for approx 12 h. The resulting complexes are not soluble in water or ethanol, slightly soluble in hot dichloromethane or chloroform, and soluble in dimethylsulfoxide and cyclohexanone at 60 °C. ^{1}H NMR, ^{13}C NMR data for each of the ionic complex synthesized are gathered in the Supporting Information. A summary of the main NMR data is collected in Tables 1 and 2.

Results and Discussion

Synthesis and Characterization. The 5-(4-cyanophenylazophenyloxy)pentanoic acid (CAzPA) was prepared from 4-cyano-4′-hydroxyazobenzene following the sequence of reactions shown in Scheme 2, by diazotizacion of 4-aminobezonitrile with sodium nitrite and coupling with phenol, and O-alkylation of the phenol with methyl 5-bromopentanoate using the Williamson reaction and subsequent hydrolysis of the ester to give the acid.

The ionic complexes were prepared by addition of amine-termined PAMAM-$(NH_2)_{16}$, PPI-$(NH_2)_{16}$ dendrimers or random hyperbranched PEI polymers dissolved in dry tetrahydrofuran (THF) to a solution of THF containing the acid, following a previously described method[7] (1:1 stoichiometry between the acid and each of the N-terminal amine groups present in the dendrimers and hyperbranched polymers).

The occurrence of proton transfer from the carboxylic acid to the amine groups was confirmed by IR measurements and ^{1}H and ^{13}C NMR spectroscopy.

We observed in previous papers that amidation reaction can occur in this type of complex when heated up to the isotropic liquid state. This is undesired, because it would complicate the characterization results.[7] In order to avoid the possible amidation side reaction, Frey et al.[18] transformed the primary and secondary amines of PEI into tertiary amino groups. Following their method, we have prepared the fully methylated PEI by reaction with a mixture of formaldehyde (37%) and formic acid, and carried out a comparison between the mesogenic properties of the PEI hyperbranched polymer and its methylated derivative (PEIMe) in order to study this effect.

FT-IR Study. The formation of the salts was confirmed by the disappearance of the carbonyl absorption band of the acid at 1739 cm^{-1} for CAzPA and the appearance of two bands in the ranges 1550−1600 and 1403−1413 cm^{-1}, depending on the ionic complex, that correspond to the asymmetric and symmetric stretching modes of the carboxylate group, indicating the transfer of the proton of the carboxylic acid to the nitrogen of the amine groups of the dendritic polymer and hence the formation of ionic complexes (see two examples in Figure 1). In the case of PAMAM complexes, the stretching band of the N−H bonds of the amide groups appears at 3280 cm^{-1}, and that of the amide carbonyl group appears at 1645 cm^{-1}.

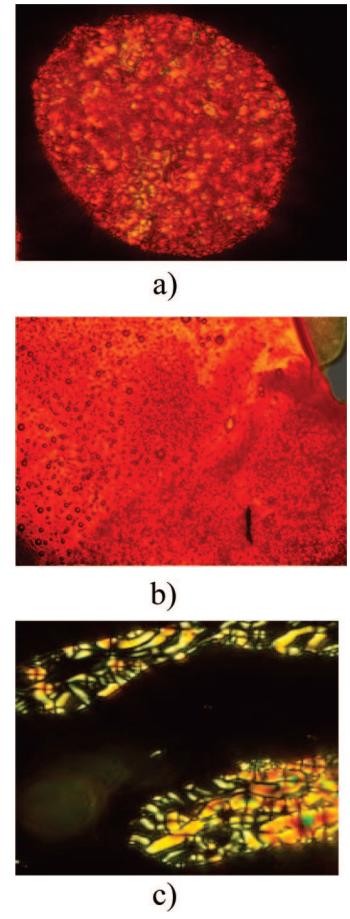


Figure 3. Optical texture of (a) a nematic drop of PEIMe-CAzPA at 125 °C (1st heating), (b) the nematic mesophase of PEI-CAzPA at 99 °C (1st heating), (c) the nematic mesophase of PEI-CAzPA at 145 °C (1st cooling) observed under the polarizing microscope (crossed polarizers).

In all the complexes, a band is observed in the interval of 2220−2224 cm^{-1} due to the cyano group. In the 5-(4-cyanophenylazophenyloxy)pentanoic acid, the absorption band corresponding to the cyano group appears at 2238 cm^{-1}, and thus, a change to lower wavenumbers occurs when the carboxylic acid is complexed with the dendritic polymers. (Main IR data of the acid and of the ionic complexes are collected in Table S1 of the Supporting Information.)

NMR Study. The compounds were also studied by NMR techniques, and the spectra were recorded in DMSO-d_6 at 333 K. The chemical structures of the ionic dendritic polymers were confirmed by one-dimensional ^{1}H and ^{13}C NMR and two-dimensional ^{1}H−^{1}H COSY and ^{1}H−^{13}C HSQC NMR. These techniques allowed us to unequivocally assign the signals. Partial 2D-HSQC spectra of the aliphatic region (1.6−3.2 ppm) of the complexes are plotted in Figure

Table 3. Transition Temperatures As Determined by DSC[a] and Thermal Stability of Acids and Ionic Complexes

compd	transitions (°C),(ΔH [J g^{-1}])	TGA analysis
CAzPA	C 117 (154.9) I	294, 76.3%
PAMAM-CAzPA[b]	g 19.4 N 140 (0.9) I	155, 5.5%; 201,12.2%; 242, 68.9%; 300, 51.7%
PPI-CAzPA[b]	g 47.4 N 163 (2.0) I	203, 5.0%; 269,49.9%; 337, 31.0%
PEI-CAzPA	C 73 (18.5) N 150[c] I	140, 5.2%; 247, 18.8%; 335, 53.6%
PEIMe-CAzPA[b]	C 62 (9.8) N 140 (1.0) I	135, 2.5%;222, 53.6%; 345, 22.7%

[a] Data from second scan, and taken in the peak. C = crystal, *g* = glass, N = nematic mesophase, I = isotropic liquid. [b] Transition peak is not observed in the cooling process. [c] Optical data.

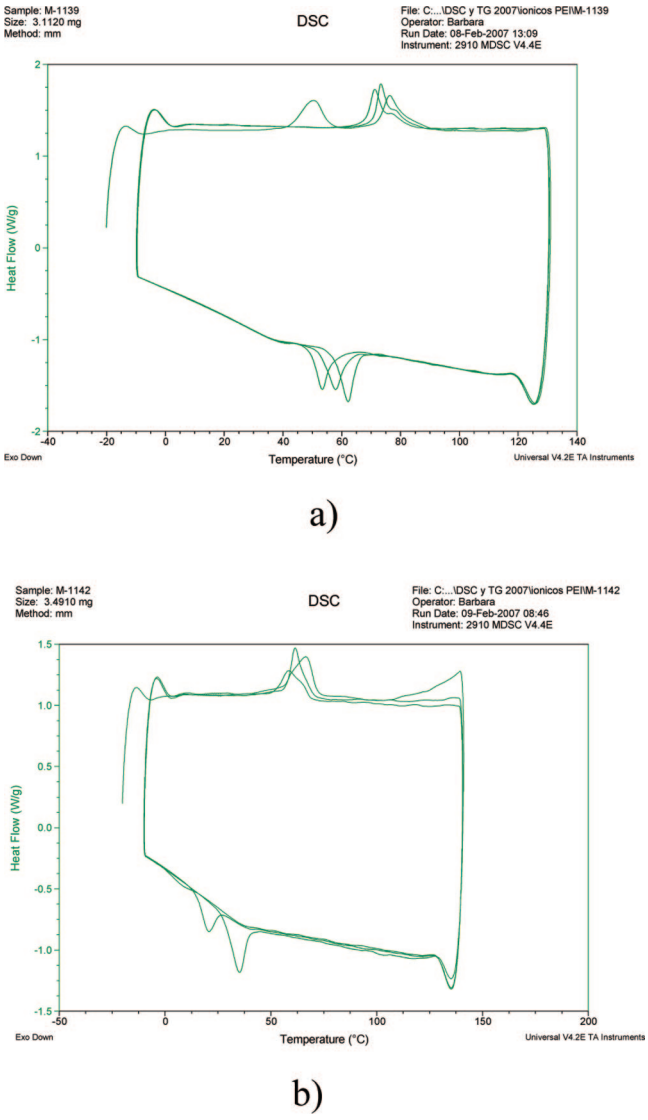


Figure 4. DSC scans at 10 °C/min for (a) PEI-CAzPA and (b) PEIMe-CAzPA.

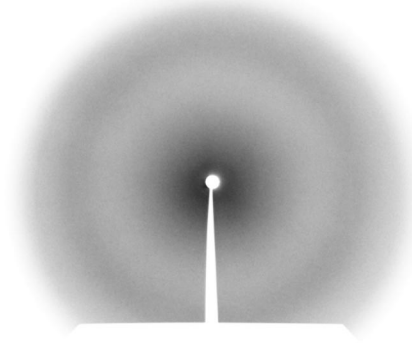


Figure 5. X-ray pattern of PEI-CAzPA in its N mesophase at 87 °C.

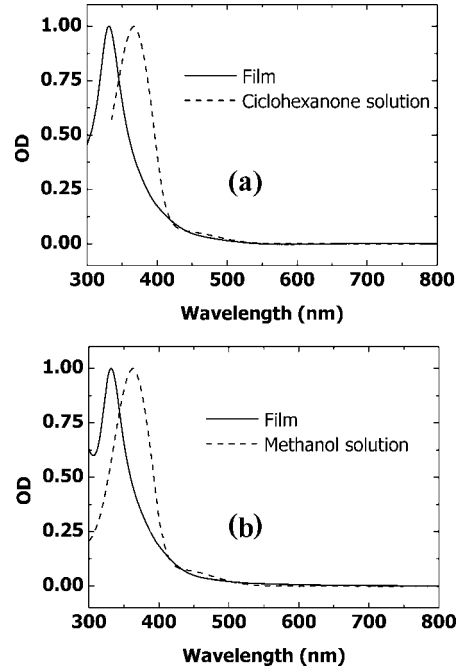


Figure 6. UV−vis absorption of (a) PEIMe-CazPA and (b) PAMAM-CAzPA in thin film and in a cyclohexanone and methanol solution, respectively.

2. The results obtained confirmed the formation of the salts; significant ^{1}H and ^{13}C NMR data of the carboxylic acid and the ionic LC dendritic polymers are gathered in Tables 1 and 2. The methylation of PEI was confirmed by NMR spectroscopy. These data agree with those reported by Frey et al., taking into account the different solvents used.[18]

The signal corresponding to the proton of the acid of the 5-(4-cyanophenylazophenyloxy)pentanoic acid disappears in the ^{1}H NMR spectra of the salts, and the ^{13}C signal of the carbon atom of the carboxylic group (δ = 173.8 ppm) is shifted between +0.7 and +1.3 ppm in the spectra of the ionic complexes. The signal of the peak CH_2 next to COO ($-\underline{CH_2}-COO^-$) in the ^{13}C NMR spectra is slightly shifted, too (0.03−1.7 ppm), with respect to the chemical shift of the acid, which confirms the ionization of the carboxylic acid.

The shifts of the cationic counterpart depend on the initial amine. This shift is more sensitive in ^{13}C NMR than ^{1}H NMR. Thus, in the PAMAM-CAzPA complex the variation of shift of the C_α to terminal amine ($-\underline{CH_2}-NH_2$) is −0.5 ppm, −0.8 ppm in PPI-CAzPA, +0.3 in PEIMe-CAzPA, and −1.3/−1.2 ppm in the PEI-CAzPA complexes, respectively. The shifts of the C_β ($-\underline{CH_2}-CH_2-NH_2$) are also pronounced: −0.7, −1.3, −2.6/−2.2 ppm in PAMAM, PPI and PEI respectively.

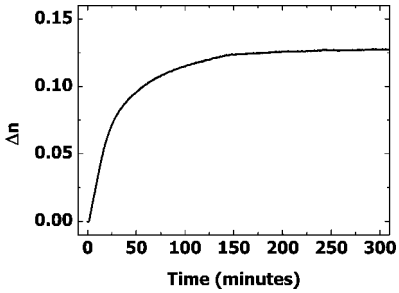


Figure 7. Photoinduced birefringence recorded in a thin film of PEIMe-CAzPA with a 488 nm linearly polarized beam (1 W/cm^2). Light is switched on at $t = 0$ min and switched off at $t = 240$ min.

Thermal Behavior. The phase behavior of the ionic dendrimers was analyzed by combination of different techniques including polarizing optical microscope (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). We have to emphasize that the 5-(4-cyanophenylazophenyloxy)pentanoic acid does not exhibit liquid crystal properties.

The identification of the liquid crystalline phase was done on the basis of POM observations. All complexes synthesized showed a nematic mesophase which was identified by the optical textures (see Figure 3) and was confirmed by X-ray diffraction. No changes in the texture were observed upon cooling the nematic mesophase for PAMAM-CAzPA and PPI-CAzPA, indicating that it freezes into a glass state, in contrast to PEI-CAzPA and PEIMe-CAzPA crystallization observed on cooling.

The transition temperatures and enthalpies that were obtained from the DSC curve of the second heating scan are listed in Table 3.

As can be observed in Table 3, by comparing the transition temperatures of the ionic complexes, the nematic mesophase interval for dendrimers (121° for PAMAM-CAzPA and 116° for PPI-CAzPA) is higher than the nematic mesophase interval for ionic random hyperbrached polymers (77° for PEI-CAzPA and 78° for PEIMe-CAzPA) which is consistent with the fact that some disorder has been introduced in the system when the molecular structure of the material is changed from a monodisperse dendrimer to a polydisperse hyperbranched polymer.

PEI-CAzPA and PEIMe-CAzPA show different thermal behavior than PAMAM-CAzPA and PPI-CAzPA. Random hyperbranched polymers show a peak of transition between the crystalline state and the nematic phase and single crystallization with supercooling in the cooling cycles (see Figure 4). However, ionic dendrimers show the absence of a crystalline state in successive heating and cooling cycles and only a glass transition to the mesophase is observed.

The thermal stability of the ionic complexes was evaluated by thermogravimetry analysis (TGA) under a nitrogen atmosphere and showed that degradation took place in several steps (Table 3). PAMAM-CAzPA showed a 5.5% weight loss at 155 °C, PPI-CAzPA showed a 5.0% weight loss at 203 °C, PEI-CAzPA showed a 5.2% weight loss at 140 °C, and PEIMe-CAzPA showed a 2.5% weight loss at 135 °C. These studies show that these materials have the main weight loss at ca. 200 °C. All the complexes lose weight at lower temperature than the carboxylic acid, but significantly above the clearing point.

Comparison of the different ionic complexes revealed that the thermal stability decreases in the direction PPI-CAzPA > PAMAM-CAzPA > PEI-CAzPA > PEIMe-CAzPA. As can be deduced from these data, in this study the ionic complexes derived from dendrimers (PPI and PAMAM) are thermally more stable than the ionic complexes derived from hyperbranched polymers.

Study of the Treated Samples of the Ionic Complexes after Three Heating and Cooling Cycles. In order to study the light decrease of the transition temperatures observed after several DSC scans, we have studied the NMR spectra of the thermally treated samples. The HSQC and COSY NMR spectra of PAMAM-CAzPA showed new signals with respect to the untreated sample; i.e., signals at 3.11 (H^y) and 2.55 (H^z) ppm in ^{1}H NMR spectrum which are correlated with 38.05 (C^y) and 47.76 (C^z) ppm in ^{13}C NMR spectrum were attributed to the formation of amide bonds (PAMAM-$\underline{CH_2}^y$-$\underline{CH_2}^z$-NH-CO-CAzPA). The percentage of amide relative to $-CH_2-NH_3^+$ groups could not be calculated due to the overlapping shifts. Only a small percentage of amide bonds have also been detected for PPI-CAzPA.

The thermal behavior of two examples (PEI-CAzPA and PEIMe-CAzPA) studied by DSC are illustrated in Figure 4. Only a discreet displacement to lower transition temperatures can be observed after the three heating and cooling cycles carried out at 10 °C/min for PEI-CAzPA complex. This effect is also observed for the methylated derivative, PEIMe-CAzPA, which could mean that the decrease of the transition temperatures is due in part to some decomposition of the complexes as a consequence of the high temperatures reached during the DSC studies.

X-ray Diffraction Studies. The nature of the mesophases exhibited by all the ionic dendritic polymers described in this paper was unambiguously assigned by X-ray diffraction at variable temperatures above their melting point. All the patterns show the usual features of a nematic phase. They contain a diffuse scattering maximum at low angles and a diffuse halo at high angles. These diffuse maxima arise from intermolecular short-range interactions parallel and perpendicular to the molecule long axes, respectively. The low-angle scattering corresponds to a local density wave along the main axes of the mesogenic units and is accounted for by the existence of short-range layer fluctuations in the nematic mesophase. The wavelength of the fluctuations deduced from the patterns by applying Bragg's law is in each case comparable to the length of the mesogenic unit. The high-angle scattering corresponds to a mean distance of 4.5−4.6 Å and is typically observed for liquid crystal phases. This diffuse maximum arises from short-range lateral correlations between the mesogenic units and also, for these compounds, between the conformationally disordered dendrimer branches. The X-ray pattern of one of the dendritic polymers (PEI-CAzPA) is shown in Figure 5.

Optical Studies. The UV−vis absorption spectra corresponding to thin films of PEIMe-CAzPA and PAMAM-CAzPA after thermal treatment (heating up to 100 °C for

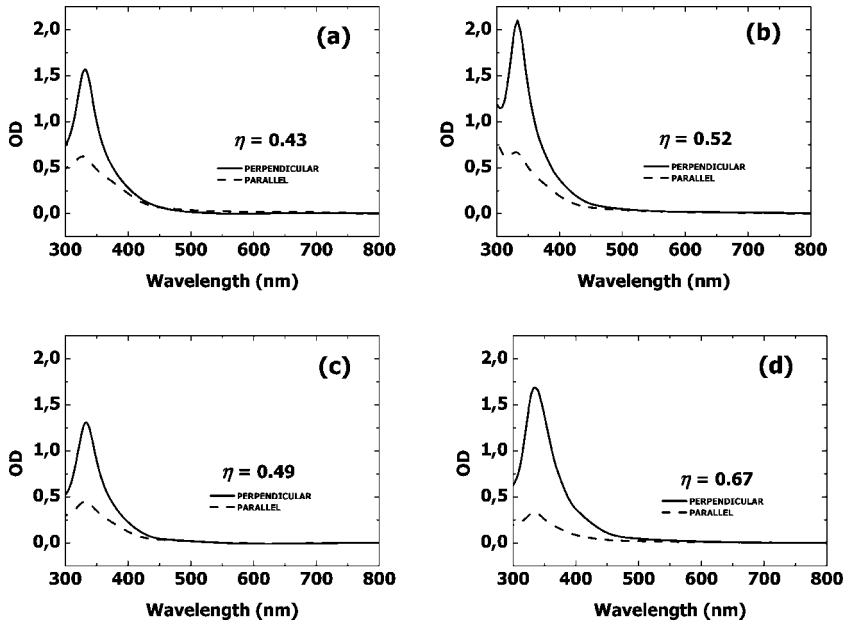


Figure 8. Equilibrium polarized absorption spectra and in plane order parameter η after irradiation with 488 nm linearly polarized light: a) PPI-CAzPA, b) PAMAM-CAzPA, c) PEI-CAzPA and d) PEIMe-CAzPA.

10 min and fast cooling down to room temperature) and solutions of the same compounds in cyclohexanone and methanol, respectively, are shown in Figure 6. Spectra of the rest of the materials (PPI-CAzPA and PEI-CAzPA) are qualitatively similar to that of PEIMe-CAzPA; therefore, only the one corresponding to this last material is shown. The absorption of the PEIMe-CAzPA cannot be measured at wavelengths shorter than 335 nm due to the strong absorption of cyclohexanone. The UV−vis spectrum of the solution shows a main absorption band at about 365 nm, associated with the $\pi-\pi^*$ transitions of the trans azo moiety. This spectrum also shows a shoulder at 450 nm assigned to the $n-\pi^*$ transition of the same moiety. The spectra of the films show noticeable, distinct features: A strong blue-shift of the main absorption band (335 nm) is observed when going from the solution to the solid state. On the other hand, the shoulder at longer wavelengths associated with the $n-\pi^*$ transition does not appear in the solid state. Significant changes in the absorption spectra of solutions and films have also been described in ISA complexes by Faul et al.[24] They have associated, in that case, the blue shift of the maximum of the $\pi-\pi^*$ absorption band in the film as compared with solution to the formation of H-aggregates of azobenzene units.

Birefringence has been induced using 488 nm linearly polarized light (1 W/cm^2) in thin films of the ionic dendritic polymers. Photoinduced anisotropy has been extensively reported in azobenzene-containing materials. It is well-known that it is generated due to the preferential orientation of azobenzene chromophores perpendicular to the light polarization direction through trans−cis−trans photoinduced isomerizations cycles.[27] Figure 7 shows the photoinduced birefringence using 488 nm linearly polarized light in a film of PEIMe-CAzPA between crossed polarizers using a diode laser beam (780 nm) as a probe. Birefringence is slowly built up upon 488 nm light irradiation. The low sensitivity observed using 488 nm can be due to the low absorption of the films at this wavelength. Irradiation at shorter wavelengths or incorporation of chromophores with absorption bands in this region could improve the dynamic of the recording process. When 488 nm light is switched off, birefringence evolves during several hours until it reaches a stable value that is higher than the one obtained during irradiation. This increase in birefringence is associated with reorientation of the chromophores due to thermotropic processes.[28] The final birefringence value is stable for several weeks as has been reported for other ISA complexes.[24]

We have also performed dichroism measurements in all the films after birefringence has reached a saturation value. The results are shown in Figure 8. We define an in-plane order parameter η as $\eta = (A_\perp - A_{||})/(A_\perp + A_{||})$

$A_{||}$ and $A_\perp$ are the optical absorptions at the 335 nm maximum measured with light linearly polarized in the direction parallel and perpendicular to the polarization of the exciting 488 nm light, respectively. High and stable values of the in-plane order parameter up to 0.67 have been reached in these materials in the recording conditions used.

Conclusions

In conclusion, we have described simple noncovalent supramolecular systems which exhibit nematic liquid crystal properties, using dendritic polymers. The method is based on the formation of ion pairs between a carboxylic acid group and the terminal amine groups of PPI, PAMAM, PEI, and PEIMe. The resulting structures are nematic thermotropic LC as revealed by X-ray diffraction and POM. The results reported herein indicate that these systems obtained by self-assembly of a rodlike promesogenic group and dendritic

(27) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 41.

(28) Kidowaki, M.; Fujiwara, T.; Morino, S.; Ichimura, K.; Stumpe, J. *Appl. Phys. Lett.* **2000**, *76*, 1377.

polymers help the formation of a nematic mesophase in contrast with our previous work where most of the ionic homodendrimers formed by spontaneous assembly of long-chain carboxylic acids or (mono, di, or tri)alkoxybenzoic acids onto the surface of amino-terminated poly(propylene imine) and poly(amidoamine) showed lamellar mesomorphism (smectic A).

This is the first time that we observe a nematic mesophase in a PAMAM-functionalized dendrimer (ionic or covalent). This could be associated with the presence of the azo group of the carboxylic acid.

Stable birefringence has been induced using 488 nm linearly polarized light in thin films of the ionic dendrimers. Stable in-plane order parameters as high as 0.67 have been reached in some of these materials. These properties together with the simplicity and versatility of the synthetic methodology make these complexes very attractive for different optical applications.

Acknowledgment. This work has been supported by CICYT-FEDER Spanish Projects MAT2005-06373-CO2-01 and CTQ2006-15611-CO2-01 and by the Gobierno de Aragón. Carlos Sánchez is grateful to MCYT and European Social Fund for support under the Ramón y Cajal program.

Supporting Information Available: Synthesis and analytical data of the intermediates and the ionic complexes. Table S1 (main IR data) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM800382Y