2660 *Macromolecules* **2010**, *43*, 2660–2663
DOI: 10.1021/ma902766j

Macromolecules
COMMUNICATION TO THE EDITOR

Ionic Photoresponsive Azo-Codendrimer with Room Temperature Mesomorphism and High Photoinduced Optical Anisotropy

Silvia Hernández-Ainsa,[†] Rafael Alcalá,[‡] Joaquín Barberá,[†] Mercedes Marcos,*[,†] Carlos Sánchez,*[,‡] and José Luis Serrano[§]

[†]Departamento de Química Orgánica, Facultad de Ciencias-Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, C./Pedro Cerbuna 12, 50009-Zaragoza, Spain, [‡]Departamento de Física de la Materia Condensada, Facultad de Ciencias-Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, C./Pedro Cerbuna 12, 50009-Zaragoza, Spain, and [§]Instituto de Nanociencia de Aragón, Universidad de Zaragoza, Pedro Cerbuna 12, 50009-Zaragoza, Spain

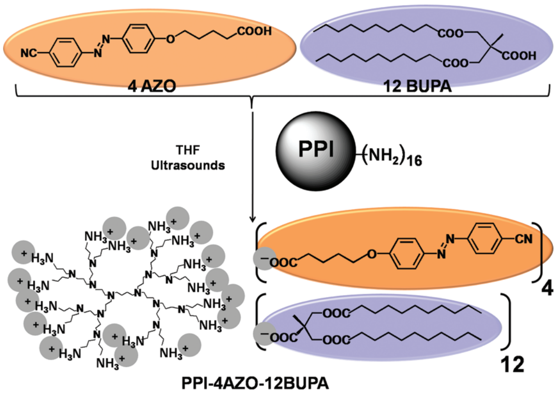
Received December 15, 2009
Revised Manuscript Received February 4, 2010

In the last few years, dendrimers have attracted increased interest due to their monodisperse branched structure[1] that, apart from enhancing solubility and decreasing viscosity compared to linear systems, allows the introduction of a higher number of active moieties with specific properties of interest in applications in such diverse fields as medicine, biology, chemistry, materials science, and engineering.[2] On the other hand, noncovalent interactions, such as H-bonding, metal-coordination, and electrostatic interaction are being intensively studied due to their capability to assemble building blocks yielding self-organized supramolecular materials.[3] In particular, ionic linkage[4] appears as a simple and versatile way to design dendrimers supporting specific functions in their periphery. Furthermore, the ionic attachment of certain organic molecules to the dendrimer surface has demonstrated to provide liquid crystal (LC) behavior,[5] even when nonmesogenic building blocks are employed.[5a] This is explained in terms of microsegregation phenomena[6] produced between the dendrimeric core and the ionically linked peripheral moieties. This allows access to a wide variety of LC structures whose dimensions can be fine-tuned with an appropriate choice of the constituent building blocks.[7,6c]

The incorporation of photoresponsive units in self-assemblies allows the control of these structures by external light stimuli.[8] In this way azobenzene molecules have been incorporated, for example, in amphiphilic vesicles to photoregulate membrane permeability.[9] Azobenzene molecules themselves are promesogenic moieties that can result in LC phases, whose orientation can be controlled by the use of polarized light showing large and stable photoinduced anisotropy[10] as compared with similar amorphous materials. This property has been thoroughly explored due to its potential applications in volume holographic storage, optical processing, or liquid crystal alignment.[11]

A simple and straightforward way to obtain both, LC and photoactive properties in a dendrimer, is by ionic linkage of several appropriated moieties, originating a combined material. We have recently reported the photoinduction of optical anisotropy in liquid crystal ionic homodendrimers containing azobenzene moieties.[12] Despite the high and stable optical birefrigence values obtained for these materials, their poor solubility in conventional organic solvents, makes it difficult to process them as thin films. To improve processability, we have synthesized a new ionic codendrimer (PPI-4AZO-12BUPA) obtained by ionically grafting of poly(propyleneimine) PPI-$(NH_2)_{16}$ (third generation) with the aromatic-based carboxylic acid 5-[4′-(4-cyanophenylazo)phenyloxy]pentanoic acid (AZO) and the aliphatic 2,2-bis(undecanoyloxymethylene)propionic acid (BUPA) (Scheme 1) (proportion AZO:BUPA 4:12). The AZO moiety was selected as the photoisomerizable group and its concentration was significantly lowered (with respect to the previously prepared homodendrimer) to favor the solubility of the material. According to our previous experience, aliphatic acids ionically grafted in PPI dendrimers result in LC behavior[5] and promote the solubility of the material. In an attempt to further enhance these properties (mesomorphism and solubility) we have selected the BUPA moiety. In fact, we have checked that the introduction of the aliphatic palmitic acid (having one single aliphatic tail), instead of BUPA in our system resulted in a highly insoluble material. This lack of solubility also appears if the quantity of AZO is increased in the codendrimer (proportion AZO:BUPA 8:8). On the other hand, since we wanted to keep enough AZO to obtain optical response, materials with lower AZO content were not explored.

Scheme 1. Synthetic Route for the Ionic Codendrimer



The codendrimer obtained by simple addition of the stoichiometric amounts of the above-mentioned moieties is liquid crystalline at room temperature (RT) and shows a broad mesomorphic temperature range (from −19 to +105 °C). The material thus prepared shows good solubility in common solvents such as dichloromethane and thin film proccesability. Photoinduced optical anisotropy has been induced in thin films of this material by using linearly polarized light. Cooperative interactions in the mesophase reinforce the achieved photoinduced order reaching a high and stable value. This is the first time that such an easy to synthesize dendrimer combines mesomorphic properties at RT, good solubility, adequate processability and large and stable photoinduced optical anisotropy.

The codendrimer has been synthesized as previously described[13] by sonication of a solution in THF of the third generation PPI commercially available dendrimer, AZO and BUPA in the appropriate stoichiometry (1:4:12). Carboxylate formation (COO^-) is demonstrated by different characterization techniques. ^1H NMR studies (Figure S2, Supporting Information) reveal that the peaks of the protons of the methylene group in α to the carboxylic group of AZO (CH_2COOH) appearing at 2.47 ppm, are shifted to 2.39 ppm in the codendrimer, because of the ionization process. On the other hand the ^{13}C NMR (Figure S3,

---

*Corresponding authors. E-mail: (M.M.) mmarcos@unizar.es, (C.S.) carloss@unizar.es.

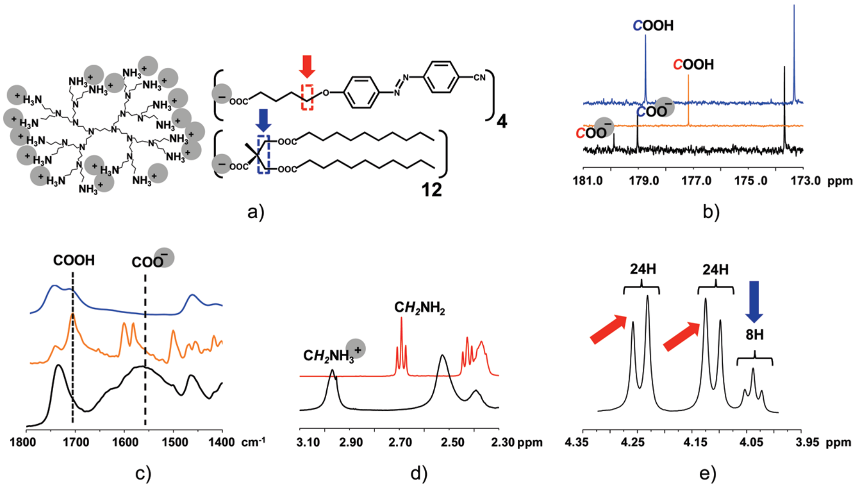


Figure 1. (a) Schematic representation of the complex. (b) ^{13}C NMR and (c) FT-IR in the range of carbonyl group of BUPA (blue), AZO (orange) and PPI-4AZO-12BUPA (black). (d) ^{1}H NMR of PPI-G3 (red) and PPI-4AZO-12BUPA (black). (e) Integration of ^{1}H NMR signals corresponding to the moieties BUPA (blue) and AZO (orange) in the PPI-4AZO-12BUPA complex.

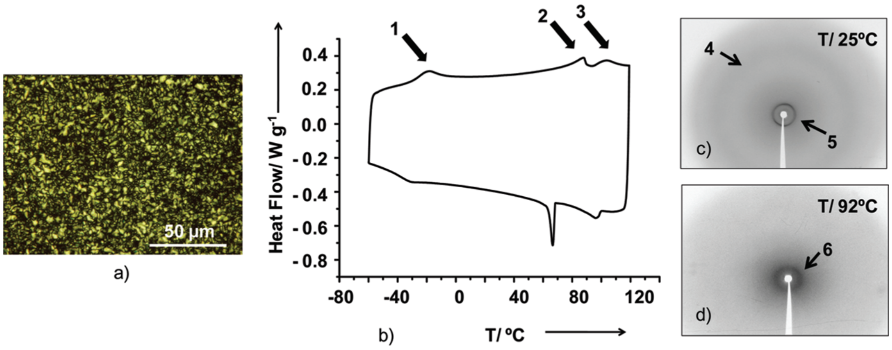


Figure 2. (a) Codendrimer POM texture observed at 43 °C in the second cooling. (b) Second DSC cycle of PPI-4AZO-12BUPA (black). (c and d) X-ray diffractograms of the codendrimer taken at 25 and 92 °C respectively in the heating process.

Supporting Information) spectrum shows the displacement of the signal of the carbon atom of the carboxylic groups (*C*OOH) of both acids from 178.7 ppm (BUPA) and 177.2 ppm (AZO) to 179.0 and 179.9 ppm respectively (Figure 1b). The disappearance of the bands corresponding to the carbonyl groups of the previous acids (1739 cm^{-1} in case of AZO and 1742 cm^{-1} for BUPA) and the existence of a band at 1562 cm^{-1} corresponding to the asymmetric stretching mode of the carboxylate group have been observed by FT-IR measurements (Figures 1c and S4 (Supporting Information)). Besides, ammonium groups ($-NH_3^+$) formation is corroborated by ^{1}H NMR, as can be deduced by the displacement of the signal of the protons of the methylene group attached to the terminal amine groups (CH_2NH_2) in the PPI dendrimer (2.70 ppm) to higher shifts (3.00 ppm) (Figure 1d) and by ^{13}C NMR because of the displacement of the signal corresponding to the C$_\alpha$ to terminal amine (CH_2NH_2) from 40.5 to 37.5 ppm in the codendrimer (figure S3). Apart from the successful formation of the ionic complex, the experimental average stoichiometry of both moieties introduced at random is confirmed by ^{1}H NMR integrated values of the signals appearing at 4.21 and 4.04 ppm. These signals correspond to protons of the methylene groups situated in α of oxygen atom ($-CH_2O-$) in the BUPA and AZO respectively (Figure 1e).

The thermal behavior of the material was studied by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Despite neither acids (AZO, BUPA), nor commercial PPI dendrimer display mesomorphic properties, the ionic interaction promotes thermotropic LC behavior in PPI-4AZO-12BUPA due to the microsegregation effect. Of special interest is that this material exhibits LC behavior from −19 °C, as the first DSC transition reveals (arrow 1 in Figure 2b) until its clearing point at 105 °C (arrow 3 in Figure 2b). Although the texture observed by POM (Figure 2a) does not change in all the range, DSC curve reveals that a phase transition takes place at 88 °C (arrow 2 in Figure 2b), that indicates the existence of a high-temperature phase. The identification of these two mesophases was performed by X-ray diffraction. The X-ray scattering (WAXS) pattern taken at 25 °C (second heating) (Figure 2c) consists of a diffuse halo in the wide angle region (arrow 4 in Figure 2c), corresponding to the distance between the conformationally disordered alkyl chains (~4.5 Å) and a sharp maximum in the low-angle region (arrow 5 in Figure 2c) related to the existence of a layered organization of the molecules, that is, the smectic phase. By applying Bragg's law a layer thickness of 30.8 Å is estimated at this temperature. However, when studying at a temperature just above the transition observed by DSC in the second heating, namely at 92 °C, this low-angle region sharp halo disappears to give a diffuse maximum (halo) (arrow 6 in Figure 2d). That is accounted for by the existence of short-range layer fluctuations typical of the nematic mesophase. It is the first time that a dendrimer containing azo moieties appears as LC in such a wide temperature range and from such a low temperature.[14]

With reference to the thermal reproducibility of the transitions, six successive DSC heating and cooling cycles at a scanning rate of 10 °C min^{-1} have been performed, and it was observed that the transition temperatures, including the isotropization one, remain almost constant, especially in the heating process (Figure S5, Supporting Information).

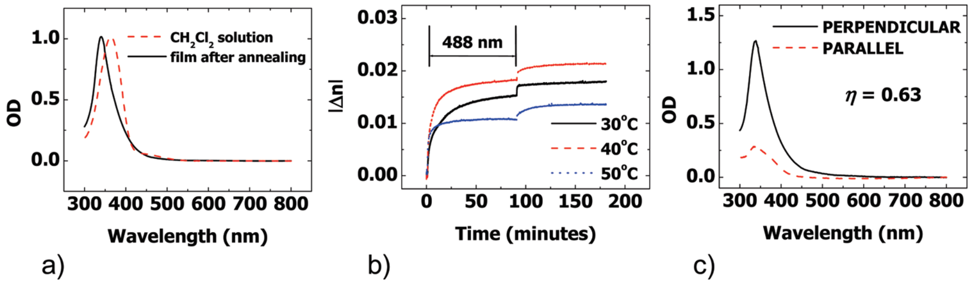


Figure 3. (a) UV−vis absorption of the dendrimer in dichloromethane and in a thin film. (b) Photoinduced birefringence recorded at different temperatures in a thin film of the dendrimer using 488 nm linearly polarized beam (900 mW/cm^2). Light is switched on at $t = 0$ min and switched off at $t = 90$ min. (c) Equilibrium polarized absorption spectra measured at RT and in plane order parameter η after irradiation with 488 nm linearly polarized light at 40 °C.

Furthermore, this material exhibits good thermal stability as shown by thermogravimetry analysis (TGA), its loss of weight becoming significant at 50 °C above the clearing point. Namely, it shows a 5.4% weight loss at 180 °C due to a partial formation of amide group (as checked by NMR and IR experiments). The onset temperature of decomposition occurs at 270 °C.

Figure 3a shows the UV−vis absorption spectrum of the dendrimer in solution (CH_2Cl_2) and in a thin film (1.2 μm thick) after thermal annealing (heating up to 120 °C for 10 min and fast cooling down to RT). The absorption spectrum of the solution shows a main absorption band at 365 nm, associated with the $\pi-\pi^*$ transition of the trans azo isomer, and a shoulder at 450 nm corresponding to its $n-\pi^*$ transition. A hypsochromic shift of the main absorption band to 340 nm is observed in the thin film after the thermal treatment. Similar changes have been observed in ionic assembled materials containing azobenzene units and have been associated with the formation of molecular aggregates (H-aggregates of azobenzene units).[8d] Photoinduced anisotropy studies using linearly polarized light of 488 nm (900 mW/cm^2) were performed in these films at different temperatures using a setup reported elsewhere (for details see Supporting Information).[15] Because of the low optical absorption of the film at the recording wavelength (OD below 0.1), the intensity of the exciting light can be considered nearly constant through the whole film thickness. Figure 3b shows the evolution of the photoinduced birefringence ($|\Delta n|$) at 30, 40, and 50 °C (birefringence was not induced when irradiated at higher temperatures). Thin films were exposed for 90 min and then kept in darkness for further 90 more minutes. In all the cases $|\Delta n|$ increases upon irradiation, the increase being faster at higher temperatures. When 488 nm light is switched off $|\Delta n|$ further increases until it reaches a saturation value. Upon cooling down to RT, birefringence further increases (not shown in Figure 3b) until a stable value is reached.

The increase of birefringence during the irradiation period is explained in terms of the isomerization and reorientation events of azo units induced by polarized light.[10b] The higher mobility of these units when temperature increases explains the increase of $|\Delta n|$ in going from 30 to 40 °C. At higher temperatures thermal disorder competes with light induced reorientation and lower values of $|\Delta n|$ are reached (experiment at 50 °C), preventing recording of birefringence at temperature of 60 °C or higher. The observed phenomenology after the irradiation period can be attributed to the liquid crystalline character of the codendrimer. When light is switched off cooperative interactions between mesogens can improve the initial order induced by polarized light. The further increase of birefringence observed when the sample is cooled down to RT is attributed to the increase of LC molecular order upon cooling. After birefringence has reached a saturation value, dichroism measurements were also performed in these films at RT. The results for the sample irradiated at 40 °C are shown in Figure 3c. Stable values of the in-plane order parameter (see experimental section) of 0.63 have been achieved in this material.

In conclusion we report in this communication on the synthesis and characterization of a new functional codendrimer obtained via ionic bonding of a commercial poly(propyleneimine) PPI−$(NH_2)_{16}$ (third generation) dendrimer with the aromatic-based carboxylic acid 5-[4′-(4-cyanophenylazo)phenyloxy]-pentanoic acid (AZO) and the aliphatic 2,2-bis(undecanoyloxymethylene)propionic acid (BUPA). It is demonstrated that the simple combination of specifically selected building blocks results in a ionic self-assembled material easy to process as a thin film, showing a broad liquid crystalline phase (more than 120 °C range) that includes room temperature and large and stable photoinduced optical anisotropy.

Acknowledgment. This work was supported by the MICINN, Spain, under Projects CTQ2006-15611-CO2-01, MAT2008-06522-C02, CTQ2009-09030, and FEDER funding EU, by seventh FP-THE PEOPLE PROGRAMME, The Marie Curie Actions—ITN, No. 215884-2, and by the Gobierno de Aragón (Project PI109/09, Research Group E04). S.H.-A. thanks the MICINN (Spain) for a grant.

Supporting Information Available: Text giving more details about the employed techniques including reaction schemes and structures, optical studies, synthesis and characterization of the materials, and DSC data, figures showing the compound structure, NMR and IR spectra, and DSC curves, and tables of temeprature data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Vögtle, F.; Richardt, G.; Werner, N. *Dendrimer Chemistry*; Wiley-VCH: Weinheim, Germany, 2009. (b) Carlmark, A.; Hawker, C.; Hulta, A.; Malkoch, M. *Chem. Soc. Rev.* **2009**, *38*, 352. (c) Newkome, G. R.; Shreiner, C. *Polymer* **2008**, *49*, 1. (d) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. Dendrimers and Dendrons: Concepts, Synthesis, Applications. Wiley-VCH: Weinheim, Germany, **2001**.

(2) (a) Boas, U.; Christensen, J. B.; Heegaard, P. M. H. *Dendrimers in Medicine and Biotechnology: New Molecular Tools*; RSC Publishing: Cambridge, U.K., 2006. (b) Fréchet, J. M. J.; Tomalia, D. A. Dendrimers and Other Dendritic Polymers; *Wiley Series in Polymer Science*; Wiley: Chichester, England, 2001.

(3) (a) Fréchet, J. M. J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4782. (b) Lim, Y.; Moon, K.-S.; Lee, M. *Chem. Soc. Rev.* **2009**, *38*, 925. (c) Imam, M. R.; Peterca, M.; Edlund, U.; Balagurusamy, V. S. K.; Percec, V. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4165. (d) Bucknall, D. G.; Anderson, H. L. *Science* **2003**, *302*, 1904. (e) Lehn, J. M. *Science* **2002**, *295*, 2400. (f) Kato, T. *Science* **2002**, *295*, 2414.

(4) (a) Binnemans, K. *Chem. Rev.* **2005**, *105*, 4148. (b) Faul, C. F. J.; Antonietti, M. *Adv. Mater.* **2003**, *15*, 673. (c) Thünemans, A. F. *Prog. Polym. Sci.* **2002**, *27*, 1473.

(5) (a) Martín-Rapún, R.; Marcos, M.; Omenat, A.; Barberá, J.; Romero, P.; Serrano, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 7397.

(b) Martín-Rapún, R.; Marcos, M.; Omenat, A.; Serrano, J. L.; Taffin de Givenchy, E.; Guittard, F. *Liq. Cryst.* **2007**, *34*, 395. (c) Marcos, M.; Martín-Rapún, R.; Omenat, A.; Barberá, J.; Serrano, J. L. *Chem. Mater.* **2006**, *18*, 1206.

(6) (a) Chandrasekar, S. *Handbook of Liquid Crystals*: Wiley-VCH: Weinheim, Germany, 1998; Vol. *2*. (b) Saez, I. M.; Goodby, J. W. *J. Mater. Chem.* **2005**, *15*, 26. (c) Cook, A. G.; Baumeister, U.; Tschierscke, C. J. *J. Mater. Chem.* **2005**, *15*, 1708.

(7) Fitié, C. F. C.; Tomatsu, I.; Byelov, D.; de Jeu, W. H.; Sijbesma, R. P. *Chem. Mater.* **2008**, *20*, 2394.

(8) (a) Kulikovsky, L.; Kulikoska, O.; Goldenberg, L. M.; Stumpe, J. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1739. (b) Kulikoska, O.; Goldenberg, L. M.; Kulikovsky, L.; Stumpe, J. *Chem. Mater.* **2008**, *20*, 3528. (c) Yu, H.; Iyoda, T.; Ikeda, T. *J. Am. Chem. Soc.* **2006**, *128*, 11010. (d) Zakerskyy, Y.; Stumpe, J.; Faul, C. F. *J. Adv Mater* **2006**, *18*, 2133. (e) Yagai, S.; Karatsu, T.; Kitamura, A. *Chem.—Eur. J.* **2005**, *11*, 4054. (f) Zhang, Q.; Bazuin, C. G.; Barret, C. J. *Chem. Mater.* **2008**, *20*, 29. (g) Xiao, S.; Lu, X.; Lu, Q.; Su, B. *Macromolecules* **2008**, *41*, 3884.

(9) Sata, T.; Shimokawa, Y.; Matsusaki, K. *J. Membr. Sci.* **2000**, *171*, 31.

(10) (a) Didehban, K.; Namazi, M.; Entezami, A. A. *Eur. Polym. J.* **2009**, *45*, 1836. (b) Nathanson, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139.

(11) (a) Hvilsted, S.; Sánchez, C.; Alcalá, R. *J. Mater. Chem.* **2009**, *19*, 6641. (b) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817. (c) Tsutsumi, O.; Kitsunai, T.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 355. (d) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847.

(12) Marcos, M.; Alcalá, R.; Barberá, J.; Romero, P.; Sánchez, C.; Serrano, J. L. *Chem. Mater.* **2008**, *20*, 5209.

(13) Chechik, V.; Zhao, M.; Crooks, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 4910.

(14) Lysachkov, A. I.; Boiko, N. I.; Rebrov, E. A.; Muzafarov, A. M.; Shibaev, V. P. *Russ. Chem. Bull., Int. Ed.* **2007**, *56*, 2407.

(15) Forcén, P.; Oriol, L.; Sánchez, C.; Alcalá, R.; Hvilsted, S.; Jankova, K.; Loos, J. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1899.