Spectrochimica Acta Part A 75 (2010) 891–900

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Star-shaped azomethines based on tris(2-aminoethyl)amine. Characterization, thermal and optical study

Agnieszka Iwan[a,*], Henryk Janeczek[b], Bozena Kaczmarczyk[b], Bozena Jarzabek[b], Michal Sobota[b], Patrice Rannou[c]

[a] Electrotechnical Institute, Division of Electrotechnology and Materials Science, M. Sklodowskiej-Curie 55/61 Street, 50-369 Wroclaw, Poland
[b] Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M. Curie-Sklodowska Street, 41-819 Zabrze, Poland
[c] Laboratoire d'Electronique Moléculaire, Organique et Hybride, UMR5819-SPrAM (CEA-CNRS-Univ. J. FOURIER-Grenoble I), INAC Institut Nanosciences & Cryogénie, CEA-Grenoble, 17 Rue des Martyrs, 38054 Grenoble Cedex 9, France

ARTICLE INFO

Article history:
Received 26 May 2009
Received in revised form
29 September 2009
Accepted 8 December 2009

Keywords:
Star-shaped azomethines
Imines
Liquid crystalline
FTIR
UV–vis
Mesomorphic behavior

ABSTRACT

The synthesis and detailed (physico)-chemical ($^1H/^{13}C$ NMR, FTIR, UV–vis and elemental analysis) characterizations of new star-shaped compounds based on tris(2-aminoethyl)amine, including in their structure an azomethine function (HC=N–) and alkoxysemiperfluorinated ($-O-(CH_2)_3-(CF_2)_7-CF_3$), octadecyloxy aliphatic ($-O-(CH_2)_{17}-CH_3$) chain or two phenyl rings (–Ph–Ph–) as a terminal group, were reported. The mesomorphic behavior was investigated by means of differential scanning calorimetry (DSC), polarized optical microscopy (POM) and additionally by FTIR(T) and UV–vis(T) spectroscopy. Wide-angle X-ray diffraction (WAXD) technique was used to probe the structural properties of the azomethines. Moreover, the azomethine A1 was electro-spun to prepare fibers with poly(methyl methacrylate) (PMMA) and investigated by DSC and POM. Additionally, a film of the A1 with PMMA was cast from chloroform and the thermal properties of the film were compared with the thermal properties of the fiber and powder. It was showed that terminal groups dramatically influence the thermal and optical properties of the star-shaped azomethines.

1. Introduction

Liquid crystalline (LC) dendrons and dendrimers present an interesting class of branched compounds. Their molecules combine structural units capable of LC mesophase formation with branched or dendritic architecture [1]. A lot of papers have been dedicated to investigate liquid crystalline properties of poly(propylene imine) dendrimers with different generations based on triphenylene [2]. However, in all papers dendrimers have been based on two or more triphenylene units as a central core [2]. Only in two papers a scientist synthesized dendritic oligoamines based on one molecule of tris(2-aminoethyl)amine [3a]. For example, Vogtle et al. [3a] obtained dendritic oligoamines via N,N-bis-sulfonylation with various sulfonyl chlorides. However, authors [3a] did not investigate the mesomorphic behavior of these compounds. Berna et al. [3b] synthesized novel monodisperse PEG-dendrons as new tools for targeted drug delivery. To the best of our knowledge LC properties of star-shaped azomethines based on one molecule of tris(2-aminoethyl)amine were first time analyzed hitherto. For this reason we decided to synthesized star-shaped azomethines having as a central core one molecule of tris(2-aminoethyl)amine and different terminal groups such as alkoxysemiperfluorinated ($-O-(CH_2)_3-(CF_2)_7-CF_3$) or octadecyloxy aliphatic ($-O-(CH_2)_{17}-CH_3$) chain or two phenyl rings (–Ph–Ph–). A special attention in our work was paid to investigate star-shaped azomethine with the alkoxysemiperfluorinated chain, because of the combination of polar and steric effects and the great strength of the C–F bond [4].

In this paper we report on investigation of the thermal behavior of star-shaped azomethines on the basis of DSC, POM techniques and vibrational spectral data. The effect of the kind of end groups (aliphatic or aromatic) on the liquid crystalline phase transitional behavior in a series of star-shaped azomethines has also been studied. We paid particular attention to the mesomorphism of the star-shaped azomethines by using FTIR(T) and UV–vis(T) techniques. The structural characterization was performed by NMR and FTIR characteristic completed via X-ray diffraction measurements and optical investigations. In this paper thermal properties of the star-shaped azomethine A1 were preliminarily studied via electrospinning technique. To the best of our knowledge the absorption properties of the star-shaped azomethines in the function of temperature were first time analyzed hitherto.

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* Corresponding author. Tel.: +48 713283061.
E-mail address: a.iwan@iel.wroc.pl (A. Iwan).

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doi:10.1016/j.saa.2009.12.030

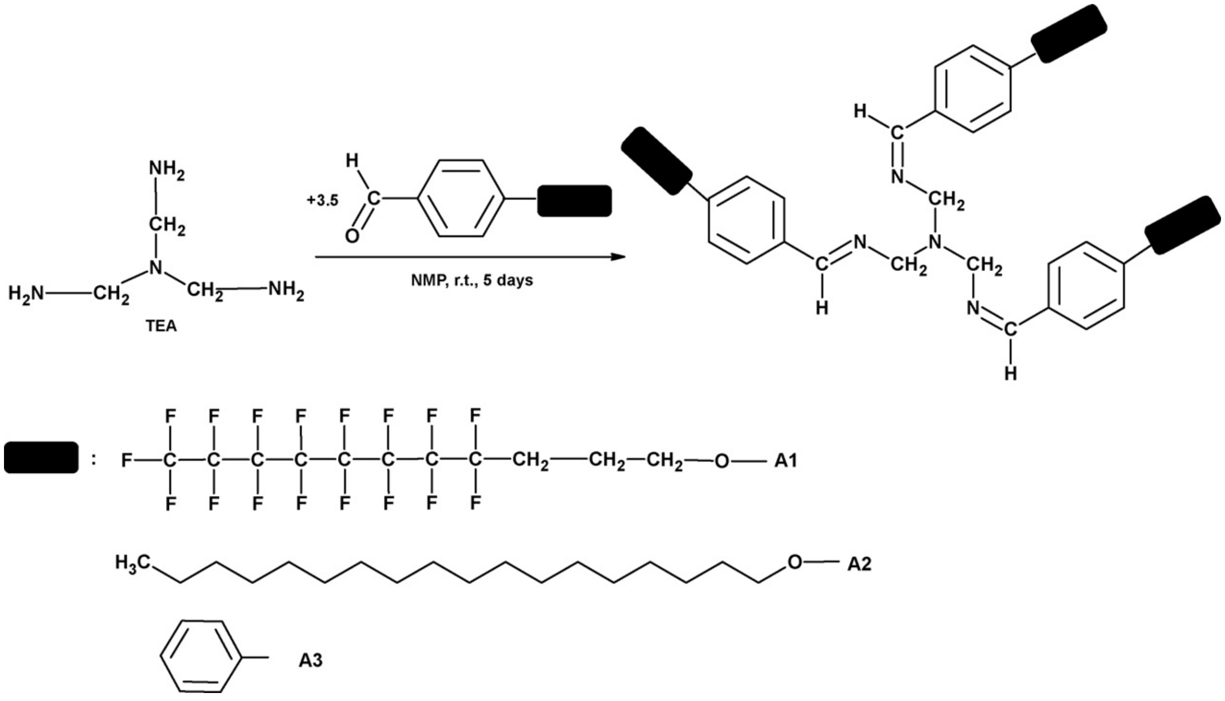

Fig. 1. Synthetic route and chemical structure of the star-shaped azomethines.

2. Experimental

2.1. General

All chemicals and solvents were of reagent grade obtained from Aldrich Chemical Co., and all solvents were dried by standard techniques. The synthesized compound was characterized by ^{1}H and ^{13}C NMR and elemental analysis. The compound was also characterized by Fourier transform infrared (FTIR) and ultraviolet-visible (UV–vis) absorption spectroscopy. NMR was recorded on a Varian Inova 300 MHz Spectrometer. Chloroform-*d* ($CDCl_3$) containing TMS as an internal standard was used as solvent. Elemental analyses (C, H, and N) were carried out by the 240C Perkin-Elmer analyzer. Infrared spectra were acquired on a DIGILAB FTS-40A Fourier transform infrared spectrometer in the range of 4000–400 cm^{-1} at a resolution of 2 cm^{-1} and for an accumulated 32 scans. Samples were analyzed in a form of films obtained after evaporating chloroform from solutions onto potassium bromide windows UV–vis absorption spectra were recorded on Hewlett-Packard 8452A spectrophotometer. X-ray diffraction patterns were recorded using powder samples on a wide-angle HZG-4 diffractometer working in typical Bragg geometry. CuK$_\alpha$ radiation was applied.

The phase transitions and mesogenicity were studied by differential scanning calorimetry (DSC) and polarizing microscope observations (POM). The textures of the liquid crystalline phases were observed with a Polarized Optical Microscopy (POM). DSC was measured on a TA-DSC 2010 apparatus using sealed aluminium pans under nitrogen atmosphere at a heating/cooling scan in a temperature range from 25 °C to over the clearing point.

FTIR spectra recorded at elevated temperatures were obtained using Carl Zeiss Jena high-temperature control equipment in the temperature range from 20 to 145 °C. The sample was heated under nitrogen at the rate of 2 °C/min and FTIR spectra were recorded by 10 °C. The same conditions were applied during cooling to 20 °C. In order to determine the quantitative relations among the bands detected in the region of 1280–1100 cm^{-1}, a WIN-IR curve fitting program was used. The initial parameters, i.e. number of peaks, centers, heights and widths of particular peaks, were obtained by analysing the second derivative spectra. An interactive procedure and Gaussian–Lorentzial fitting of curves were chosen to correct these parameters.

The temperature dependence of the UV–vis spectra was measured for thin film on the quartz (film cast from chloroform) by JASCO V-570 UV-Vis-NIR spectrometer using a temperature-controlled optical cell in a temperature range from the room temperature to clearing point in the heating process.

Electro-spinning apparatus, composed of a high voltage power supply (18 kV), a syringe pump (Prefusor Type 871102) with a glass syringe and stainless-steel blunt-ended needle (inner diameter: 0.5 mm) and a grounded electron microscope mounts as a counter electrode or a grounded flat metal collector was used. Needle and collector were mutually perpendicular, the needle being placed vertically. The solution of azomethine A1 and poly(methyl methacrylate) (PMMA) (A1/PMMA) was electro-spun using the following conditions: applied voltage of 18 kV, needle to collector distance = 18 cm with flow rate = 5.4 × 10^{-2} mL/min.

2.2. General synthetic procedure

Aldehyde (3.5 mmol) was dissolved in 1-methyl-2-pyrrolidinone (NMP) (10 ml). To this solution was added a solution of tris(2-aminoethyl)amine (TEA) (1.00 mmol, 0146 g) in NMP (10 ml). The reaction mixture was stirred at room temperature for 5 days. Then the compound was washed with ethanol and later with acetone and dried at 50 °C under vacuum for 6 h.

A1 ($N–[–CH_2–N{=}CH–C_6H_4–O–(CH_2)_3–(CF_2)_7–CF_3]_3$): yellow powder, ^{1}H NMR (300 MHz, $CDCl_3$, TMS) [ppm]: δ 8.04 (s, 3H, **CH**=N–); 7.47 (m, 6H, **HAr**–CH=N–); 6.86 (m, 6H, **HAr**); 3.65–4.06 (m, 6H, C**H**$_2$–O); 2.90 (m, 6H, –N–C**H**$_2$–); 2.27–2.35 (m, 6H, CH_2–CH_2–C**H**$_2$–CF_2); 2.09–2.17 (m, 6H, –N–CH_2–C**H**$_2$). ^{13}C NMR (75 MHz, CDCl3, TMS) [ppm]: δ 161.10, 160.90, 160.38 (–**C**H=N–), 129.59, 118.41, 114.44, 114.22, 110.73, 66.33, 60.05, 59.87, 55.79, 55.30, 28.17, 27.90, 27.62, 20.56. FTIR: ν_{max} in cm^{-1}: 3063 and 3037 (νCH), 2944 and 2920 (ν_aCH_2), 2875 and 2840 (ν_sCH_2), 1643 (νC=N), 1607, 1579, 1512, 1451 and 1422 (νPh), 1478 (δCH_2), 1372