Synthesis and Characterization of a New Thermotropic Maleimide Monomer

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Abstract: New mesogenic N-substituted maleimide monomer was obtained starting 4-maleimido benzoic acid, hydroquinone and hexadecyloxy benzoic acid by successive Schotten-Bauman By using spectral methods (IR, ^{1}H-NMR and ^{13}C-NMR) and elemental analysis the structural characteristics of the monomer were evidenced.The thermal behaviour of the monomer was followed by DSC, TGA and Polarized Light Microscopy (PLM). A good correlation was found between DSC data and PLM investigation. Thus, between 142-176^{0}C three transtions were observed, a granular smectic mesophase being evidenced at aproximately 156^{0}C.
Keywords: Maleimide monomer, thermotropic, synthesis, polarized light microscopy,(PLM).

1. Introduction

Polymers of N-substituted maleimides and their derivatives can be classified into polyimides, important high-performance engineering plastics, being a class of rigid polymers because of the imide rings in the backbone. This provides the polymers with superior mechanical and thermal stability [1].

The peculiar homo- and copolymerization characteristics of the electron-deficient maleimide group make it an attractive monomer for designing speciality vinyl polymers. Although maleimide undergoes homopolymerization with great difficulty, it copolymerizes quite readily with a variety of vinyl monomers. Further, it is known to form alternating copolymers with electron-rich monomers. Apart from enhancing the thermal stability and glass transition temperature of the resultant copolymers, maleimide group can effectively serve as a vehicle for many functional groups for their predefined distribution in a vinyl polymer backbone through free radical copolymerisation [2].

One of the main advantages offered by functional maleimides is the fact that new monomers with desired substituents to the imino nitrogen can be readily prepared [3,4].

The aim of the present work was the synthesis and characterization of new functional maleimide-type compounds containing different functional groups that allowed the attachment of a classical mesogenic moiety. This mesogenic group is of phenyl benzoate type. The *p*-n-alkoxybenzoic acids, starting with n-propyloxybenzoic acid, exhibit liquid-crystalline behavior, and their mesogenic potential increases with the length of the alkoxy group. Phenyl benzoates as mesogenic groups may impart some special characteristics to their side-chain liquid-crystalline polymers. The primary significant characteristic of the phenyl benzoate moieties may be their strong interactions governed by electronic and geometrical factors, allowing the mesogenic group

to achieve more ordered packing with respect to other mesogens [5].

2. Experimental

2.1 Materials

Maleic anhydride (Aldrich) was sublimated before use. All solvents were purified and dried by standard techniques, before to use. Acetic anhydride (Merck), *p*-aminobenzoic acid, hydroquinone (Fluka), and 4-hexadecyloxybenzoic acid (Across) (COBA) were used without further purification. Thionyl chloride (Fluka) was distilled just before use.

2.2 Preparation of intermediates and maleimide monomer

2.2.1. 4-Maleimido benzoic acid (MBA). It was synthesized by the condensation reaction of maleic anhydride with *p*-aminobenzoic acid followed by cyclodehydration using acetic anhydride and sodium acetate according to a literature procedure [6].
Yield 85%; mp 234 °C (lit. [6] mp 244 °C); IR (cm^{-1}): 3460-3200 (COOH); 3105-3100 (=CH); 1720 (O=CNC=O); 1610 (C=C); 1217 (C-O); 820 (phenyl); 720 (cis CH=CH).

2.2.2. 4-Maleimidobenzoic acid chloride (MBAC). It was synthesized according to a literature procedure [6].
Yield 73%; mp 157-158 °C (mp lit. [6] 168-169 °C); IR (cm^{-1}): 1770 (COCl); 1715 (O=CNC=O); 1600 (C=C); 700 (cis CH=CH).

2.2.3. N-[4-(4'-hydroxyphenyloxycarbonyl) phenyl] maleimide (HPPMI). It was prepared as was previously described [7].
Yield 79%; mp 208 °C; Anal. Calc. for $C_{17}H_{11}NO_5$ (%): C, 66.02; H, 3.58; N, 4.53. Found: C, 66.10; H, 3.67; N, 4.71.
IR (cm^{-1}): 3450 (OH); 3105-3100 (=CH); 1765, 1720 (imide I); 1705 (C=O ester); 1600 (C=C); 1380 (imide II); 1240 (C-O-C ester); 1190 (C-(OH) phenolic); 1150 (imide III); 1070 (ester); 840 (*p*-disubstituted phenyl).

^{1}H-NMR (δ, ppm in DMSO-d6): 9.53 (s, 1H, OH); 8.30-8.03 (q, 2H, Ar-H, *ortho* to carbonyl group); 7.64-7.59 (q, 2H, Ar-H, *ortho* to imide group); 7.25 (s, 2H, HC=CH); 7.1-7.06 (d, 2H, Ar-H, *ortho* to O atom); 6.83-6.79 (d, 2H, Ar-H *ortho* to hydroxyl).
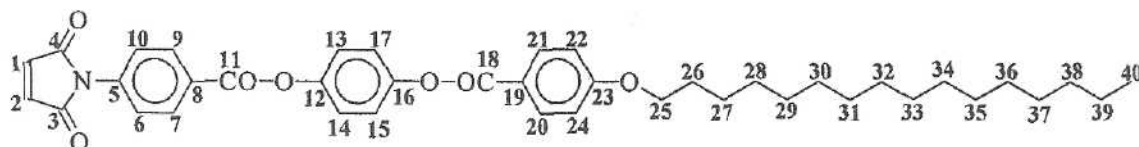
2.2.4. 4-Hexadecyloxybenzoic acid chloride (COBAC)
This acid chloride was prepared as reported previously [8].
Anal. Calc. for $C_{23}H_{37}O_2Cl$ (%): C, 72.50; H, 9.79; Cl, 9.31. Found: C, 72.72; H, 9.80; Cl, 9.43.
IR (cm^{-1}): 2900, 2860 (CH aliphatic); 1760 (COCl); 1600 (C=C aromatic); 1460 (CH$_3$); 1280 (C-O-C); 1170 (CH$_2$ chain); 840 (*p*-disubstituted phenyl).
^{1}H-NMR (δ, ppm from TMS in CDCl$_3$): 8.08-8.04 (d, 2H, aromatic), 6.96-6.92 (d, 2H aromatic); 4.06-4.01 (t, 2H, Ar- O-CH_2-); 1.83-1.78 (t, 2H, Ar-O-CH$_2$-CH_2-); 1.7-1.25 (m, 26H, -(CH_2)$_{13}$-); 0.87-0.85 (t, 3H, CH$_3$).

2.2.5. 4'-{[4"-(Hexadecyloxy)benzoyl]oxy}phenyl 4-maleimidobenzoate (COBAMI). The mesogenic monomer was obtained by a esterification reaction between HPPMI and COBAC as was previously described [8].

Yield 66%; mp 156 °C. Anal. Calc. for $C_{40}H_{47}NO_7$ (%): C, 73.48; H, 7.25; N, 2.14. Found: C, 73.57; H, 7.32; N, 2.15.
IR (cm^{-1}): 3105-3050 (*cis* =CH maleimide); 2920, 2850 (aliphatic); 1770 (imide I); 1708 (imide I; C=O ester); 1610 (C=C, aromatic and maleimide); 1420 (CH$_3$); 1400 (imide II); 1260 (C-O-C ether); 840 (*p*-disubstituted phenyl); 830 (*cis* =C–H maleimide); 695 (imide IV, carbonyl ring deformation).
^{1}H-NMR (δ, ppm from TMS in CDCl3): 8.32-8.29 (d, 2H of C20 and C21); 8.16-8.12 (d, 2H of C7 and C9); 7.61-7.58 (d, 2H of C6 and C10); 7.3-7.26 (m, 4H of C13, C14, C15, C17); 6.99-6.96 (d, 2H of C22 and C24); 6.9 (s, 2H of C1 and C2).
^{13}C-NMR (δ, ppm in CDCl3): 168.82 (C3, C4); 164.77 (C11); 164.208 (C18); 163.617 (C23); 148.369 (C12, C16); 136.12 (C5); 134.46 (C1, C2); 132.33 (C7, C9), 131.08 (C20, C21); 128.318 (C8); 125.25 (C6, C10); 122.52 (C13, C14, C15, C17); 121.36 (C19); 114.368 (C22, C24); 68.42 (C25); 31.9 (C38); 29.65-29.40 (C28-C34); 29.33 (C35, C36, C37); 29 (C26); 25.96 (C27); 22.68 (C39); 14.09 (C40). (see Scheme 1)

Scheme 1 Structure of COBAMI

2.3 Characterization
^{1}H-NMR and ^{13}C-NMR spectra of 5-10% (w/w) solutions in CDCl3 or DMSO-d6 as solvents were recorded at room temperature at 250 and 62.85 MHz, respectively, on a Bruker DPX 250 spectrometer. Tetramethylsilane was used as the internal standard. The 2D heteronuclear correlated (HETCOR) spectra were recorded at 62.89 MHz by using a sweep width of 10 KHz and 128 scans with 4K data points.
IR spectra were recorded on a Shimadzu IR-470 Infrared spectrophotometer using films cast from CH$_2$Cl$_2$ solutions on NaCl pellets.
Thermal characteristics of the polymers were obtained from measurements performed with a Mettler TA 4000 instrument. It consisted of a differential scanning calorimeter DSC-30, a TGA-50 furnace with a M3 microbalance and TA72 GraphWare software. DSC was calibrated by measuring the melting point of indium, zinc and lead standards for temperature scale and melting enthalpy of indium for heat flow scale. Specimens of 6 to 11 mg were used. Measurements were carried out under a nitrogen flow rate of 80 ml·min^{-1} according to the following protocol: first, second and third heating scans from 0 to 170 °C at 10 °C·min^{-1}; fourth heating from 0 to 300 °C at 10 °C·min^{-1} after ageing one day at ambient conditions; first cooling (quenching) from 170 to 0 °C at 100 °C·min^{-1}; second and third cooling from 170 to 0 °C at 10 °C·min^{-1}.

The formation of liquid-crystalline phases was confirmed by cross-polarized optical microscopy observations with a Reichert Polyvar microscope equipped with a programmable Mettler FP52 heating stage.

3. Results and discussion

3.1. Synthesis of N-phenylmaleimide monomer COBAMI
The 4-maleimidobenzoic acid, a very versatile reagent, was often used in the last decade to obtain different N-phenyl maleimide [6-9] or bismaleimide monomers [9,10].
As was previously reported [7], we used the same reagent for the synthesis of the HPPMI intermediate (Scheme 2). The ^{1}H-NMR spectrum of the hydroxyl-containing intermediate is presented in Figure 1.
Then, by a classical Schotten-Baumann condensation with 4-hexadecyloxybenzoic acid chloride (COBAC), the maleimide monomer COBAMI was obtained.
The structure of this new monomer was confirmed by infrared, ^{13}C- and ^{1}H-NMR spectroscopies as well as by elemental analysis (see experimental part). In particular, the 2D HETCOR spectrum of COBAMI shows cross signals between the peaks at 134.46, 132.33, 131.08, 125.25, 122.52, 114.368, 68.41, 29.65-29.33, 29, 25.96, 22.68 and 14.09 ppm in the ^{13}C-NMR spectrum and those at about 8.3, 7.6, 7.28, 6.99 and 6.9 in the [1]H-

NMR spectrum. The latter signals were attributed respectively to protons or carbons C1, C2, C7, C9, C20, C21, C6, C10, C13, C14, C15, C17, C22, C24, C25, C28-C37, C26, C27, C39 and C40 and protons on them, respectively [8].

Owing to its structure with both hydrophilic and hydrophobic groups, the new monomer is soluble in moderate concentrations in a large variety of solvents, the best solubility being qualitatively observed in chlorinated ones. It is insoluble in non-polar solvents such as hexane, heptane, and cyclohexane.
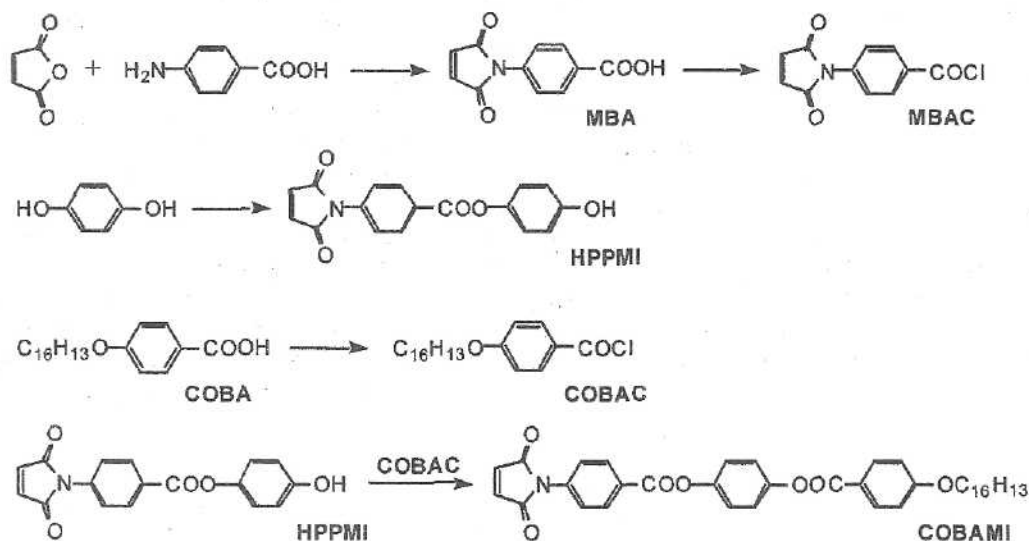
Scheme2. Reaction pathway for the synthesis of monomer COBAMI

3.2. Thermal behavoiur of the monomer COBAMI

Prior to investigation of the liquid crystalline properties of the monomer, it was analyzed by thermogravimetric analysis (TGA).

Monomer COBAMI decomposed in nitrogen atmosphere in two overlapping steps of weight loss leaving ca. 21 wt-% residue at 680 °C. The former step of weight loss was ca. 3 wt-% at an onset temperature (T_{on}) of ca. 269 °C defined at a slope of -0.048%/K and the latter was at 346 °C at -0.053%/K [8].

The DSC traces for the first heating, the first cooling and the second heating are presented in Figure 2. In the second heating three endotherms corresponding to three transitions could be observed. The first one was attributed to the transition from the crystalline state to the melted one. A granular smectic mesophase take place at approximately 156°C that is corresponding to the maximum of the second endotherm. The phase transition from smectic to nematic is presented in Figure 3 b). The nematic texture was evidenced by PLM at 165°C (Figure 3 c)
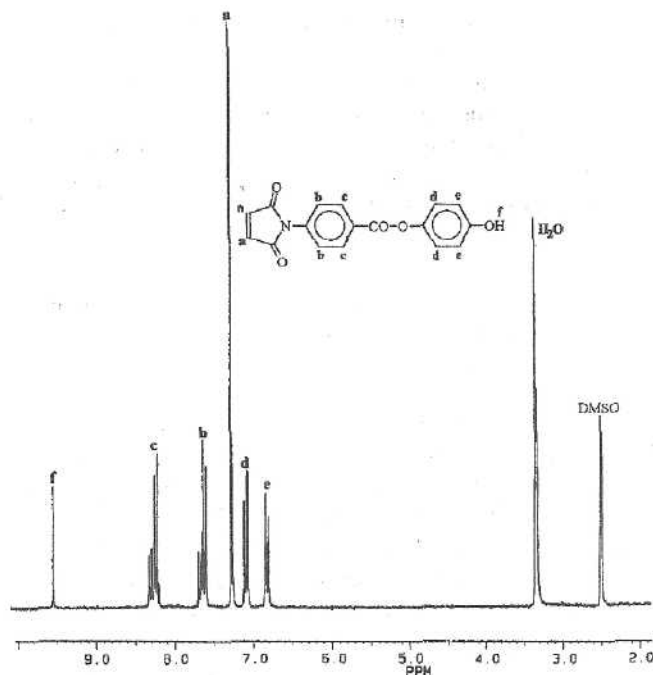

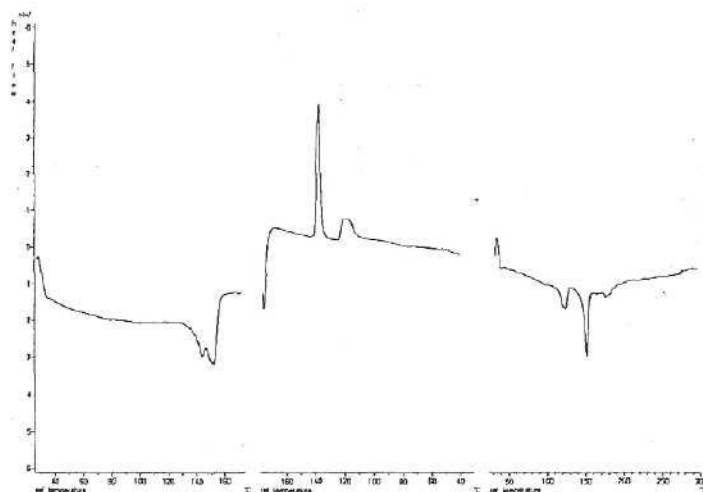Figure 1. The H-NMR spectrum of the intermediate HPPMI in DMSO-d₆
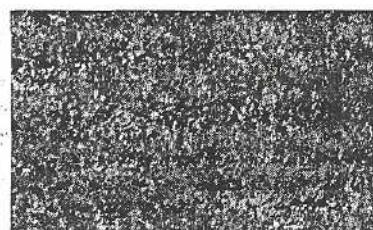
Figure 2

4. Conclusions

Different compounds belonging to the N-phenyl substituted maleimide class containing various functional groups (carboxyl, chlorocarbonyl, hydroxyl) were synthesized and characterized. These functional groups allowed the attachement of a mesogenic moiety as the side group in a maleimide type monomer. By spectral methods , the proposed structures were confirmed and the DSC data were correlated with the PLM investigations.
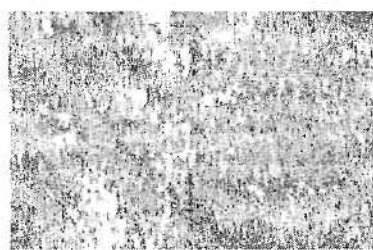
Figure 3. (a) The granular smectic mesophase; (b) The phase transition from smectic to nematic; (c) The nematic texture at 165°C
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5. References

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