

Dedicated to Prof. Bogdan C. Simionescu
on the occasion of his 75th anniversary

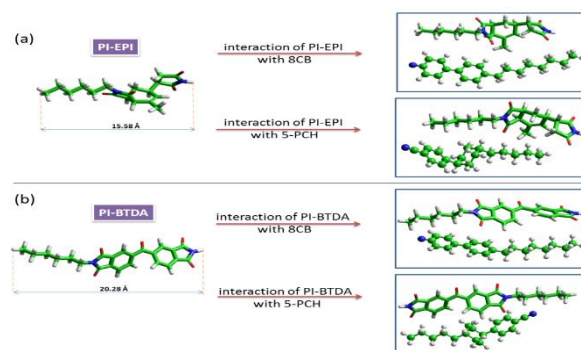
DIANHYDRIDE MOIETIES INVOLVEMENT ON THE INTERACTIONS OF SOME POLYIMIDES WITH NEMATIC COMPOUNDS

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This article has the aim to perform a comparative analysis between a semi-aromatic polyimide (PI) and a fully aliphatic one, with focus on the dianhydride moiety effect on certain physical properties of interest in display applications. Molecular modeling proved that the distinct PI conformational features have implications on the polymer interaction with the nematic molecules. Optical studies indicate different levels of transparency as a function of the aromatic extent of the sample structure. For achievement of the nematic orientation on the PI layers, their surface is subjected to mechanical erosion. The characteristics of the created topography reveal the involvement of the type of dianhydride used in the PI synthesis. Wettability data show a relevant enhancement in the nematic adhesion work values after the surface rubbing of both PIs.



INTRODUCTION

Over the years, thermostable polymers have been introduced in many technologies, including in space vehicles, light emitting diodes, transistors energy storage, displays, and other electronic devices. A special attention is attributed to polyimides (PIs), which have the advantage of good film forming properties, chemical resistance, combined with mechanical toughness, relatively flat surface and outstanding dielectric characteristics.^{1–3} Based on these features, PIs can be utilized as anisotropic and flexible components for display devices, namely as orientation supports for nematic molecules.⁴ For such purposes, it is paramount to investigate the material optical performance, together with the surface

morphology and wettability behavior. Related to the optical properties, it is highly desirable to attain high transparency and compatible refractive index to that of the liquid crystal (LC).⁵ Generally, PIs with completely aromatic structure have the deficit of powerful inter-molecular interactions (charge transfer complex (CTC)), which render weak processability in most solvents and brownish color, thus enhancing the light absorption in the visible domain.⁶ To prevail over this inconvenience, researchers are focused on the adaptation of the polymer structural design to reduce the CTC. This can be accomplished by inserting non-symmetrical and flexible linkages (that weaken the chain co-planarity), bulky groups and low polarizable elements (*i.e.* aliphatic segments, fluorinated units).^{7–11}

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On the other hand, in a LC display, the PI film is placed in contact with a nematic substance that must gain proper alignment to ensure the desired device operability. Therefore, the polymer topography must be adjusted to generate uniform orientation of the LC molecules. Several techniques are employed to produce surface modification of the PI films for this scope, namely soft-lithography,¹² photo-aligning procedures¹³ and mechanical abrasion with materials of variable malleability.^{14,15} The first two methods present limitations in terms of texturing area and photo-definable polymer structures, respectively. The rubbing approach is more facile, cheaper and leads to topography characteristics that are very stable in time. Given these benefits, such PI mechanical treatment is currently applicable at industrial level.

Another relevant aspect arises from the ability of the nematic substance to spread on the surface of the PI support.¹⁶ To understand the performance of a PI structure, it is necessary to perform wettability studies to evaluate the level of adhesion at the interface between the polymer and LC molecules. These aspects have significant implications on LC anchoring onto the surface of the textures PI support.¹⁷ The chemical structures of both nematic and PI are affecting the extent of the interfacial spreading.¹⁸

This article intends to analyze the influence of PI structure on the compatibility with nematic substances. A comparative study is made by selecting two PIs having a common aliphatic diamine, namely hexamethylenediamine (HMD) that reacted to either a cycloaliphatic dianhydride (4-methyl-6-[(2,5-dioxotetrahydrofuran)-3-yl]-3a,6,7,7a-tetrahydroisobenzofuran-1,3-dione (EPI)) or an aromatic one (4,4'-carbonyldiphthalic acid anhydride (BTDA)). The synthesis and structural characterization of these PIs is published in former articles, which pursued either PI blood compatibility,¹⁹

flexible supports for electronics²⁰ or achievement of textured layers by combined rubbing and stretching for nematic orientation.¹⁷ Here, the studies are continued by pursuing novel aspects, such as the influence of the dianhydride moieties on the interactions of some PIs with some nematic substances utilized in LC display manufacturing. Molecular modeling was done to clarify the conformational changes induced by the type of the dianhydride moiety in the presence/absence of the LC. The selected PI structures are textured here by mechanical abrasion with a harder material (sandpaper) and their morphology is studied by optical microscopy. Wettability tests enabled the analysis of the nematic interfacial interaction with the chosen PI layers.

RESULTS AND DISCUSSION

Molecular modeling

Simulation of the polymer structures by means of specific software facilitates understanding of their conformational characteristics, while extracting basic physical and chemical parameters. The optimized PI structures are depicting the configurations achieved at the smallest free energy. Figure 1 shows that the structure based on EPI dianhydride is more flexible than that containing BTDA dianhydride moiety. This is supported by the attained values of the distance between the ends of the chain, which for PI-EPI is 15.58 Å, while for PI-BTDA is 20.28 Å. This could be attributed to the C-C single bond between the imide and aliphatic ring from EPI unit, which renders enhanced freedom degree in comparison to the BTDA residues. The quantitative structure-activity relationships (QSAR) characteristics are collected from simulations, enabling the correlation of the chemical structure with certain properties.²¹

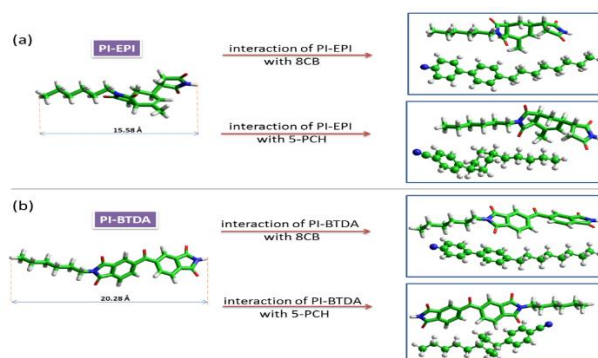


Fig. 1 – Simulation data illustrating geometry optimization at lowest energy in vacuum for: a) PI-EPI; b) PI-BTDA polymers and their corresponding binary complexes with 8CB and 5-PCH compounds, respectively. The polymer structures are represented by tube shape and those of the LCs are denoted by balls and cylinders.

For the analyzed polymers and their LC systems, the following QSAR properties are determined: van der Waals-surface-bounded molecular volume (V_w), molar refractivity (R) and polarizability (P). Table 1 lists the computed values. The calculations reveal that the semi-aromatic PI-BTDA sample exhibits a larger V_w , along with a higher polarizability and refractivity in comparison to the data attained for the wholly aliphatic PI-EPI sample. Such features are reflected in the optical performance of these PIs. Moreover, molecular dynamic computations grant the assessment of the energy profile of interactions between the selected PIs and the following nematics: 4'-octyl-4-biphenylcarbonitrile (8CB) and 4-trans-pentylcyclohexyl cyanobenzene (5-PCH). The semi-empirical approach, relying on the Parametric Model 3 (PM3) for the quantum computation of the molecular structure, facilitates the deduction of the interaction energy in the systems constituted by the PI and the chosen nematic molecules. The interaction energy (noted E_i) for each considered PI/LC pair is achieved starting from single point estimations of the optimized complexes. In this way, monitoring the

LC influence on the polymers is performed. The collected data are also summarized in Table 1. Considering the Mulliken charges and common chemical properties, the possible configurations of the PI/nematic systems were computed and optimized to extract the E_i energy by accounting on the relation (1):²²

$$E_i = E_{\text{polymer/LC}} - (E_{\text{polymer}} + E_{\text{LC}}) \quad (1)$$

where, $E_{\text{polymer/LC}}$ is the PI/LC binding energy of the complex, E_{polymer} is the binding energy of either PI-EPI or PI-BTDA, E_{LC} is the binding energy of LC (8CB or 5-PCH).

When two compounds begin to interact, it is known that a higher magnitude of E_i is ascribed to a higher binding energy and conformational stability. For both PIs, the interaction energy is slightly smaller for the systems containing 8CB, whereas the E_i parameter is a little larger when PIs are found in the presence of the 5-PCH nematic. Given the small differences between the E_i values for both LCs, it can be concluded that both polymers interact very well with the chosen nematics.

Table 1

The estimated QSAR parameters and thermo/physical properties for PIs, LCs and PI/LC systems

Sample/system	V_w [\AA^3]	R [\AA^3]	P [\AA^3]	Binding energy [kcal/mol]	E_i [kcal/mol]
PI-EPI	319.38	92.60	36.17	-5198.11	-
PI-BTDA	347.74	109.13	41.86	-5640.95	-
8CB	299.79	89.30	35.89	-4655.47	-
5-PCH	278.59	80.94	31.70	-4470.12	-
PI-EPI: 8CB	624.54	177.13	72.06	-9898.44	-44.10
PI-EPI: 5-PCH	603.39	170.81	67.87	-9712.12	-43.89
PI-BTDA: 8CB	647.95	192.63	77.75	-10330.80	-34.38
PI-BTDA: 5-PCH	626.78	186.05	73.56	-10147.01	-35.94

Refractivity and transmittance

The refractive index of the polymers can be predicted based on the group theory using the Lorentz-Lorenz formula (2):

$$R_u = V_u(n_R^2 - 1)/(n_R^2 + 2) \quad (2)$$

where n_R is the refraction index, R_u and V_u are the molar refraction and molar volume of the structural unit.

Both molar refraction and molar volume are assessed by utilizing the principles of the group contribution approach, where the units composing the polymer structure are collected from the literature.²³ The R_u and V_u values of the samples are comprised in Table 2. The type of the inserted

dianhydride affects the refractive properties of the imide-containing polymer. A higher polarizability of the chemical sub-structures forming the PI is responsible for a larger molar refraction, while the flexible character of the macromolecule is affecting the magnitude of the volume. The attained data from Table 2 show that a larger R_u/V_u ratio is indicative of a higher refractive index, as noted in the case of the PI-BTDA. This is supported by literature data,²⁴ which reveal that PIs containing BTDA display high polarizability reflected in high dielectric constant and implicitly bigger refractive index. Conversely, when inserting a cycloaliphatic dianhydride, like EPI, with weaker polarizability and bigger flexibility, the R_u/V_u ratio is smaller and the refractive index is lower. This is also in agreement with other reports.^{5,18}

Table 2

The assessed molar refraction, molar volume, the R_u/V_u ratio, refractive index and transmittance (at 589 nm) values for the PI samples

PI code	R_u [cm ³ /g]	V_u [cm ³]	R_u/V_u	n_R	T_{589} [%]
PI-EPI	83.865	236.414	0.354	1.628	94.30
PI-BTDA	104.982	287.282	0.365	1.652	94.00

The transmittance at 589 nm can be evaluated starting from the refractive properties of the material, according to the Fresnel relation. As noticed in Table 2, the radiations at 589 nm are propagating in a higher amount when passing through the PI-EPI sample (with reduced CTC) in comparison to the one containing BTDA unit. It seems that the PI with cycloaliphatic segments is more transparent in regard to the semi-aromatic one containing BTDA. This is confirmed by the recorded UV-VIS-NIR spectra depicted in Fig. 2, which reveal at 589 nm slightly lower values for the measured transmittance (in comparison to the estimated data) due to the small absorption caused by low coloration, which is not foreseen by the applied theoretical model.

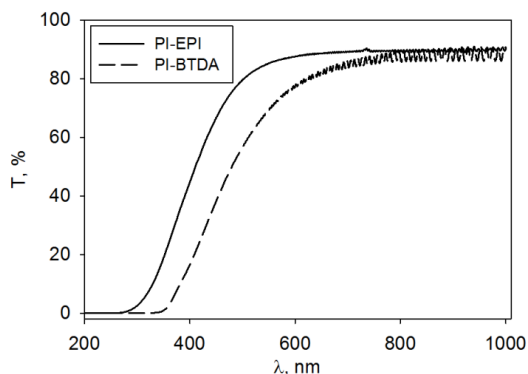


Fig. 2 – The transmittance variation with wavelength for PI-EPI and PI-BTDA films.

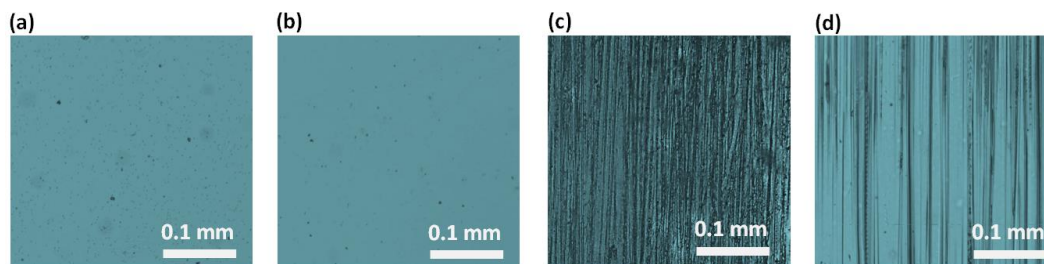


Fig. 3 – Micrographs of pristine: a) PI-EPI; b) PI-BTDA; c) rubbed PI-EPI; d) PI-BTDA.

Polyimide interaction with 8CB nematic

Polymer wettability is important when evaluating the adhesion of a substance deposited onto its surface. In order to analyze the performance of the pristine and textured PI supports, the work of adhesion with 8CB nematic is estimated with the formula (3):

$$W_{ad} = \gamma_n(1 + \cos\psi) \quad (3)$$

where W_{ad} is the adhesion work, ψ is the PI contact angle with LC, and γ_n is the nematic surface tension.

Upon measuring the contact angles of the LC drops placed on the PI supports, the data were inserted in the formula (3) and the results are summarized in Table 3.

Optical microscopy

The morphology at macro-level of the PI layers is examined under an optical microscope. The surface of both imide-containing polymers, before applying any treatment, is relatively flat and has negligible defects, as viewed in Figs. 3(a and b). For acquiring the desired surface anisotropy of the polymer support (which is essential for LC alignment), the PI surface was subsequently modified by abrasion with sandpaper. The original isotropic topography is converted into an ordered one, composed of parallel micro-trenches. The depth is expected to be deeper in comparison to that of the trenches created by abrasion with textile materials.¹⁷ The uniformity of the generated traces is not the same for the examined PI films, as remarked in Figs. 3(c and d). The rigid PI chains containing aromatic BTDA dianhydride moieties cannot follow so easy the imposed deformation during mechanical treatment, thus the texture uniformity is less obvious. Oppositely, the flexible cycloaliphatic EPI dianhydride moiety enhances the ability of the corresponding PI chains to orient during the mechanical abrasion, rendering denser and more uniform micro-trenches on the PI film surface, which is useful to induce nematic alignment.^{5,17}

Table 3

The contact angle of 8CB on the pristine/rubbed PI films and adhesion work.

Pristine PI	ψ [°]	W_{ad} [mN/m]	Rubbed PI	ψ [°]	W_{ad} [mN/m]
PI-EPI	60	64.80	PI-EPI	41	75.80
PI-BTDA	56	67.36	PI-BTDA	49	71.54

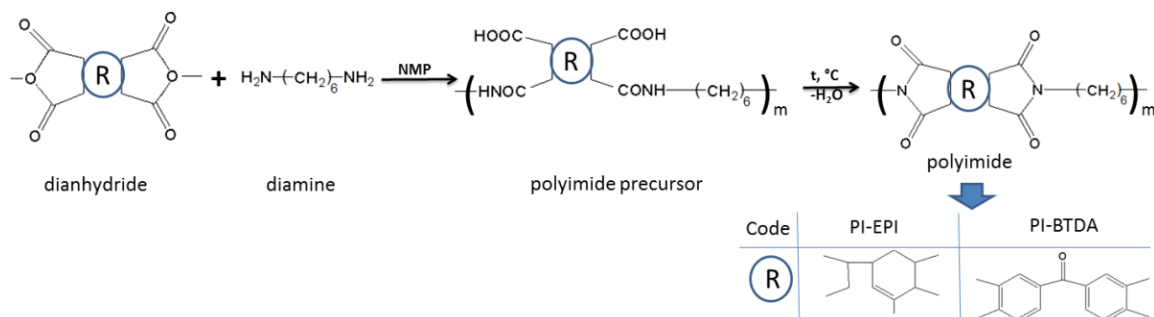
Both pristine PI films display high contact angles (over 60°), while after surface abrasion the values of ψ are decreasing. Hence, after the PI surface rubbing, the adhesion forces are enhanced so that the nematic is better spread on the textured polymer layer. The polar dianhydride BTDA moiety renders smaller contact angle for the pristine film, but after texturing, its rigid character impedes the chains to orient in a large extent during mechanical deformation and ψ decreases with a smaller rate. Even if initially PI-EPI had less adhesion to 8CB, after rubbing, the flexible EPI based structure allowed higher orientation of the PI chains, which favored improved LC adherence to the modified surface of PI-EPI. This was also proved in a previous work for another polymer structure.²⁵

EXPERIMENTAL

The discussed polymers were attained by a two-stage polycondensation reaction in anhydrous N-Methyl-2-pyrrolidone (NMP) solvent, between the hexamethylenediamine (HMD)

with either 4-methyl-6-[(2,5-dioxotetrahydrofuran-3-yl]-3a,6,7,7a-tetrahydroisobenzofuran-1,3-dione (EPI) or 4,4'-carbonyldiphthalic acid anhydride (BTDA). Each reaction involved equimolar amounts of diamine and dianhydride reactants and the processes were carried out under nitrogen atmosphere. Initially, the monomers were stirred for several hours at 25°C rendering a viscous polyimide precursor solution in NMP. Next, the reaction mixture was deposited on glass slides and the temperature was gradually enhanced (~270°C) for ensuring the thermal imidization process. The detailed synthesis and structural characterization of the evaluated polyimides were previously described in other works [19, 20]. Finally, the PI films were removed from the glass slides via soaking in water and followed by drying. Scheme 1 displays the synthesis routes of the analyzed PIs and the attributed codes.

The surface of the polyimide films was adjusted by unidirectional rubbing with sandpaper using a lab-designed device, as detailed in another work.¹⁵ The nematic LCs used in this study are: 4'-octyl-4-biphenylcarbonitrile (8CB) and 4-trans-pentylcyclohexyl cyanobenzene (5-PCH). Molecular modeling of the polyimide and the selected nematic substances is accomplished on Hyperchem8 (Demo version). Optical microscopy examinations were done on a Bresser instrument in ambient conditions. Transmittance was measured on a Specord 210 Plus system. Contact angles were attained on a lab-made system with a video-based element and fine syringe.



Scheme 1 – The illustration of the chemical route of the PI synthesis and the attributed codes.

CONCLUSIONS

The article intended to clarify the involvement of the dianhydride type on the conformational, optical and wettability properties of studied PI/LC systems. Molecular modeling elucidated that the distinct flexibility and polarizability of the dianhydride unit slightly affects the PI/LC interaction. Optical transmittance is higher when CTC interactions are low, as noted for PI-EPI. During rubbing, the dianhydride flexibility is essential for attaining a uniform texture and proper wettability as desired for LC orientation.

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