

New polymeric materials for photonic applications: Preliminary investigations



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ABSTRACT

In this paper we propose two types of polymeric materials synthesized by us suitable to interact by assembling with DNA in order to obtain new NLO biomaterials. The first polymer is a methacrylic chromophore with azobenzene groups and carbazolyl sequences known for their carrying principles while the second one is a copolymer of the methacrylic chromophore with a N-substituted amide. The N-substituted amide is N-acryloyl morpholine already used in biological application and also because is compatible with DNA.

Spectral characterization of these materials showed charge transfer interactions depending on the solvent. The results obtained indicate that these new polymeric/copolymeric chromophores could interact with DNA in order to obtain biomaterials for photonic applications.

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1. Introduction

Recent studies showed that DNA functionalized with CTMA represent a good matrix for photonic applications [1–4].

A new direction to functionalize DNA is the carbazole containing polymers class. A large attention is paid to this kind of polymeric materials due to their potential application in the optical field [5]. Another interesting class suitable for photonic applications is represented by azo derivatives [6,7]. When this kind of sequence (azo group) is introduced in polymer architectures the structural flexibility of the substituents must have the necessary space for the reversible switch process anti-sin-anti [8], which is in fact an inversion of substituents that goes by unbond–rebound of the azo bond.

The materials assemble based on the carbazole and azo sequences will have a response at an external stimulus like heat, light, etc. and perhaps they will be able to produce a chemical transformation induced by energy. In these materials the rotational or translational degree of freedom is given by the weak bonds. The control and the reversibility of the molecular motions require knowing of the conformational landscape: the interaction between the interlocked parts and the characterization of the relative movement.

The best way to obtain such polymers is to control the synthesis having in mind the applications and the desired properties of the final materials. These well define structured materials ((co)polymers) can self-assemble or be pre-assembled in various morphologies. This can be a new way to design synthesis as a macromolecular engineered synthesis process [9].

Because of its optical properties induced by the double helix structure, DNA has the potential to orient the photonic chromophores with nonlinear optic properties. Thus, chromophoric molecules, can intercalate between the nucleic bases (perpendicularly on the helix axis) or to lie parallel with the helix (spiral form) [3,10,11]. Moreover the compatibility of carbon/hydrogen based organic semiconductors with biomolecules makes them suitable for bio-organic semiconductors devices which can be used for living organisms [1,12].

DNA and amides can interact by chemical bonding or complexes and it is expected that by introducing N-acryloyl morpholine (NAM) in chromophoric polymers a new kind of interaction can be obtained. This interaction could be a new type of complexation forming a triple helix with the DNA [13,14].

In order to obtain new materials we synthesized two chromophoric monomers with methyl methacrylate polymerizable group link to an ethyl carbazolyl sequence modified with the azobenzene group. The differences between these two monomers are the substituents at the azobenzene sequence: for the first one we have nitro group as substituent and for the second one has two cyan groups as substituents [15].

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In this work a spectral characterization performed on two polymeric chromophores (poly MECNO₂ and poly MEC(CN)₂) and copolymers of these two materials with NAM is presented. This study showed that these new materials could interact with DNA in order to obtain biomaterials for photonic applications.

2. Materials and methods

N-acryloyl-morpholine (NAM) and was purchased from Aldrich and purified by distillation under reduced pressure.

The chromophoric monomers used in this study were MECNO₂ and MEC(CN)₂ (Fig. 1b) synthesized in agreement with the method published by Angiolini et al. [16,17]. The polymerization and copolymerization were realized by dilatometry technique using as initiator lauroyl peroxide (PL) purchased from Aldrich and purified by recrystallization from ethanol. The solvent used for polymerization and copolymerization was 1,4-dioxane from Aldrich, which was purified by distillation over LiAlH₄. Diethyl ether was used as precipitation agent and it was purchased from Chimopar SA.

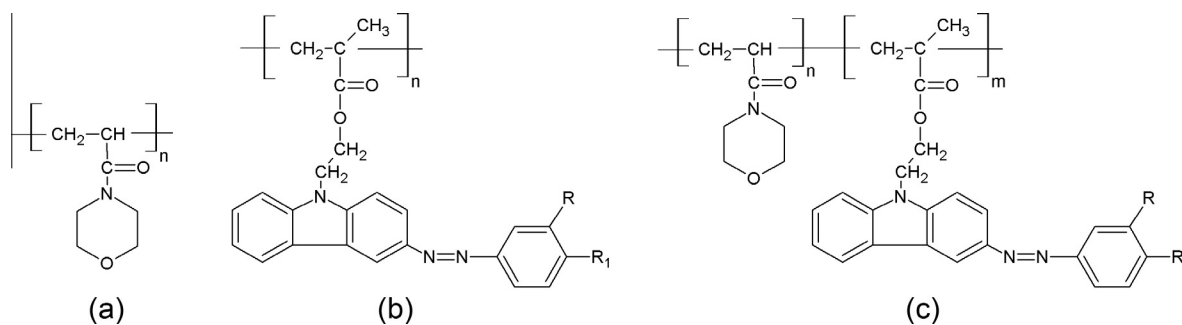


Fig. 1. (Co)polymers structures: (a) poly NAM, (b) poly MECNO₂ (R₁ = H; R = NO₂) and poly MEC(CN)₂ (R = R₁ = CN) and (c) poly (MECNO₂-co-NAM) (R₁ = H; R = NO₂) and poly (MEC(CN)₂-co-NAM) (R = R₁ = CN).

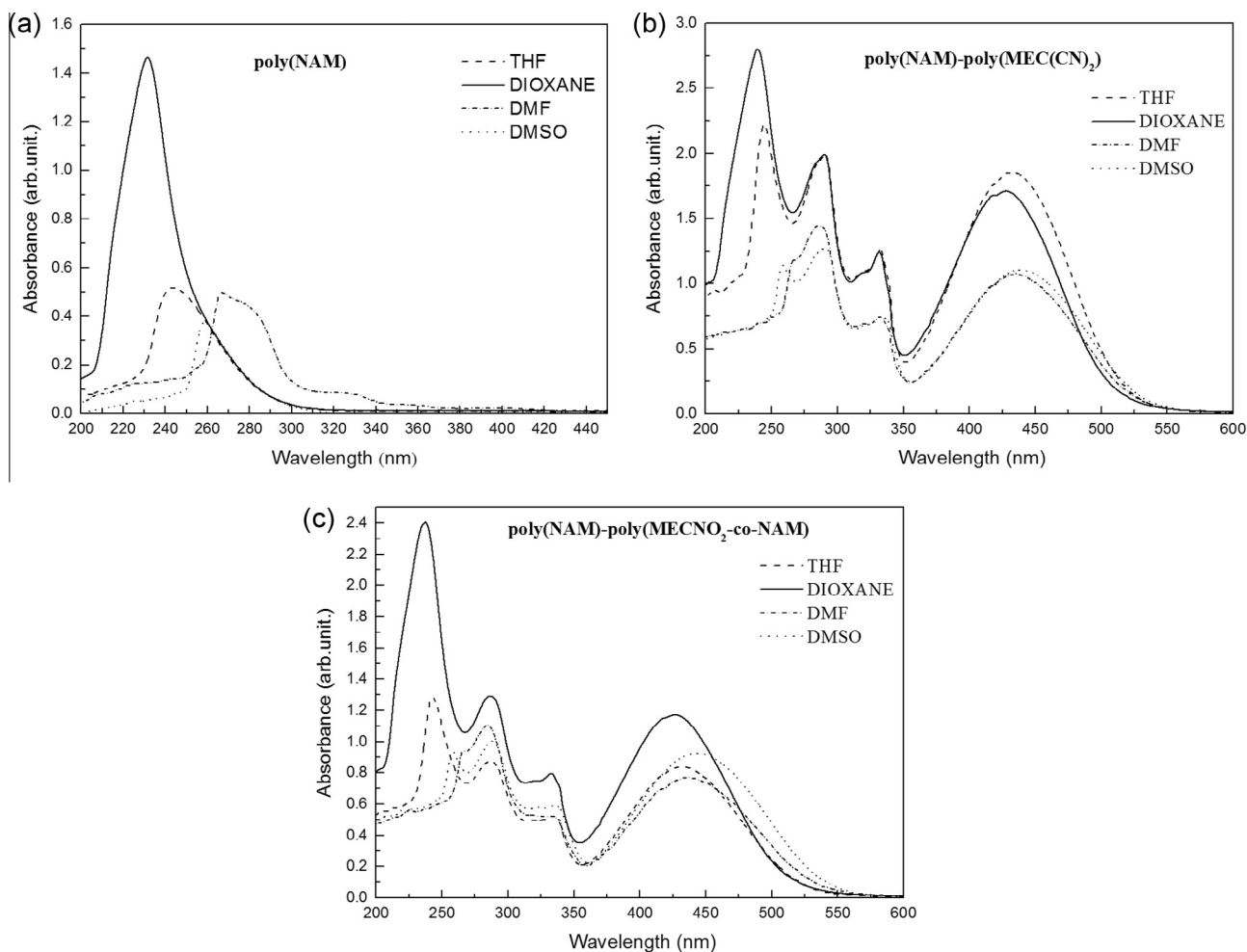


Fig. 2. UV-Vis absorption spectra of: (a) poly NAM, (b) poly NAM-poly MEC(CN)₂, (c) poly NAM-poly MECNO₂-co-NAM.

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