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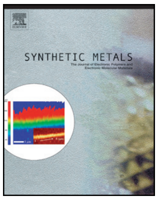

Photopolymerization of pyrrole/methacrylate mixtures using α-cleavage type photoinitiators in combination with iodonium salt

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ABSTRACT

Hybrid systems formulated with pyrrole and methacrylate monomers were photopolymerized with both UV ($\lambda = 365$ nm) and visible ($\lambda = 470$ nm) light. It is known that conducting polymers produced by electrochemical or chemical synthesis are intractable solids or powders which display poor mechanical properties and low processability. An advantage of the photopolymerization process is that it allows processability and mechanical properties of final polymers to be optimized by incorporating flexibilizers and different additives into photopolymerizable formulations. Mixtures pyrrole/methacrylate were photoactivated with the iodonium salt *p*-(octyloxyphenyl)phenyliodonium hexafluoroantimonate (Ph_2ISbF_6), in combination with 2,2-dimethoxy-2-phenylacetophenone (DMPA), 2-methoxy-2-phenylacetophenone (BZME) or the pair camphorquinone (CQ)/ethyl-4-dimethylamino benzoate (EDMAB). The Ph_2ISbF_6 in combination with DMPA or BZME was an efficient photoinitiator system under irradiation at 365 nm. Conversely, in mixtures photoactivated with Ph_2ISbF_6/CQ/EDMAB the polymerization of both pyrrole and methacrylate was comparatively slow. Microscopy studies revealed the absence of phase separation indicating that the mixtures pyrrole/methacrylate resulted in the formation of an interpenetrating polymer network. The electrical conductivity of the hybrid polymers increased markedly with the amount of polypyrrole as a result of the formation of a conducting polymer network in the insulating BisEMA matrix.

1. Introduction

Organic conducting polymers such as polypyrrole have attracted increasing attention over the last two decades for applications of technological interest including the manufacture of rechargeable batteries [1], corrosion prevention coatings [2], printed circuit boards [3] conducting inks [4] and polypyrrole-coated silver nanoparticles with antibacterial activity [5]. Most of the π-conjugated electronically conducting polymers, including polypyrrole, are synthesized by either electrochemical [6–8] or chemical processes [9–12]. Electrochemical oxidation of pyrrole forms a film of conducting polymer at the electrode surface while chemical synthesis proceeds via the oxidation of pyrrole with an oxidant such as ferric chloride [9]. The polymer produced by these methods is generally an intractable solid or powder which displays poor mechanical properties and low processability. Several attempts have been made to improve the mechanical properties of polypyrrole by forming blends or composites with other polymers. Electrical semi-conducting composites have been prepared by the polymerization of pyrrole inside porous polymethylmethacrylate [13], poly(vinyl alcohol) [14] and poly(vinylchloride) matrixes [15]. Migahed et al. [16] synthesized conducting composites by polymerization of pyrrole in ethylene-vinylalcohol copolymer. Recently, Takano et al. [17] prepared conductive films based on pyrrole-cellulose acetate.

Despite the extensive results published on chemical and electrochemical polymerization of pyrrole, reports on the photochemical polymerization are relatively scarce [18–23]. An advantage of the photopolymerization process is that it allows mechanical properties of polymer films to be optimized by incorporating different additives and flexibilizers into photopolymerizable formulations. The objective of this study was to examine the photoinduced polymerization of pyrrole in combination with a methacrylate monomer. Polymeric materials based on mixtures pyrrole/methacrylate have the potential to combine the electronic conductivity of polypyrrole with the simplified processing procedures and attractive mechanical characteristics of methacrylate polymers. To the authors' knowledge, there have been no reports on the simultaneous photopolymerization of

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pyrrole and methacrylates. Methacrylate monomers are readily photopolymerized by a free radical mechanism while pyrrole polymerizes by a cationic mechanism. The selected pyrrole/methacrylate system was photoactivated with an iodonium salt in combination with 2,2-dimethoxy-2-phenylacetophenone, 2-methoxy-2-phenylacetophenone and the pair camphorquinone/ethyl-4-dimethylamino benzoate. The extent of reaction of the individual monomers was followed by UV–vis spectroscopy and Fourier transform infrared in the mid region (MIR). Conversion values at the surface of thick specimens (~2 mm) were evaluated by attenuated total reflectance (ATR). Electrical conductivity of photocured mixtures was assessed.

2. Experimental

2.1. Materials

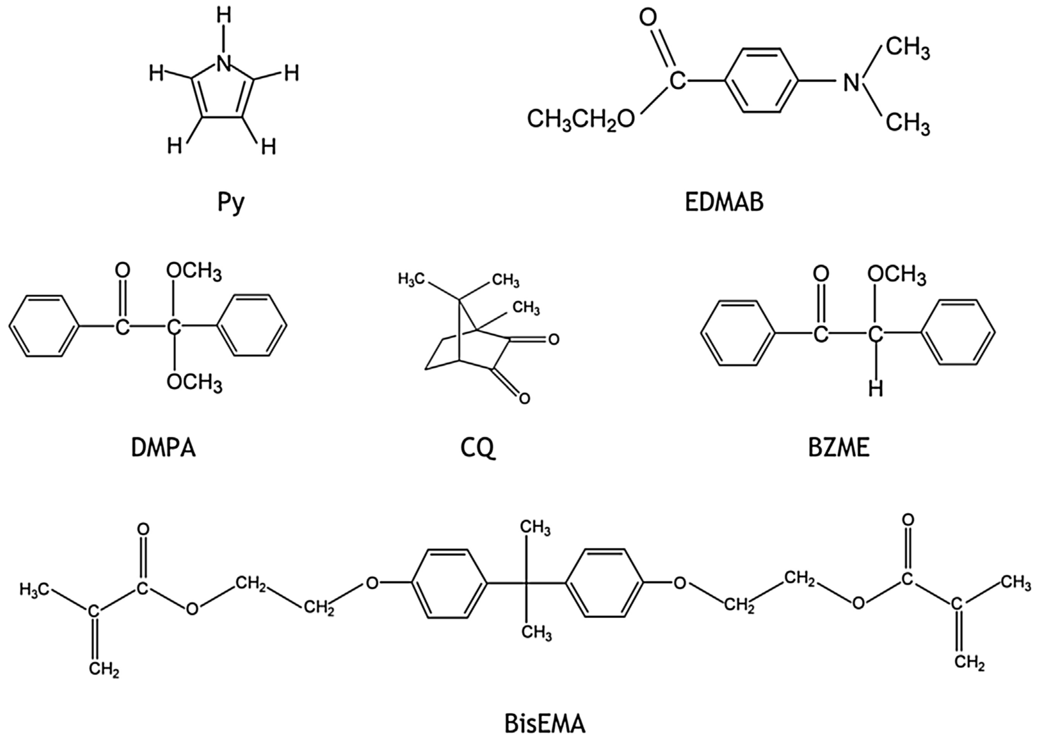
Pyrrole (Py) (Sigma–Aldrich, Buenos Aires, Argentina) was distilled twice under reduced pressure and stored in a refrigerator at about 5 °C before use. The methacrylate monomer 2,2-bis[4-(2-methacryloxyethoxy)phenyl]propane (BisEMA) was from Esstech, Essington, PA. The iodonium salt was *p*-(octyloxyphenyl)phenyl-iodonium hexafluoroantimonate (Ph_2ISbF_6) (OMAN 071, Gelest Inc., Philadelphia, USA). The free radical photoinitiators 2,2-dimethoxy-2-phenylacetophenone (DMPA), 2-methoxy-2-phenyl-aceto phenone (BZME), camphorquinone (CQ) and ethyl-4-dimethyl aminobenzoate (EDMAB) were from Sigma Aldrich, Buenos Aires, Argentina. All materials were used as received. The structure of the monomers and photoinitiators is shown in Scheme 1.

Two light emitting diodes (LEDs) light sources were used in the present study. These LEDs were selected because their spectral irradiances overlap with the absorption spectra of DMPA, BZME and CQ. Mixtures Py/BisEMA containing DMPA and BZME were irradiated with a LED with its emmitance centered at 365 nm. The intensity of this LED was set at three different values by varying the electrical voltage through the semiconductor: 75, 135 and 175 mW/cm^2. The mixtures pyrrole/methacrylate photoactivated with the pair CQ/EDMAB were irradiated with a LED unit (Valo, Ultradent, USA) with a wavelength range 410–530 nm and irradiance equal to 600 mW cm^{-2}. The absolute, total intensity of the LED sources was measured with the chemical actinometer, potassium ferrioxalate, which is recommended for the 253–577 nm wavelength range.

2.2. Methods

The absorption spectra of mixtures Py/BisEMA were measured with a UV–vis spectrophotometer (1601 PC, Shimadzu) at room temperature (*ca* 20 °C). UV–vis studies in an air environment were carried out in 0.5 ± 005 mm thick samples sandwiched between two disposable 1 mm thick quartz plates. The formation of polypyrrole was followed using the changes in absorbance at the wavelength of its maximum absorption. The molar absorption of DMPA and BZME in BisEMA at 365 nm are 167 (l/mol cm) and 110 (l/mol cm) respectively. The molar absorption of CQ in BisEMA at 470 nm is 42 (l/mol cm).

Fourier transform infrared (FTIR) spectra were acquired with a Nicolet 6700 Thermo Scientific in transmission mode. Mid-infrared (MIR) spectra were acquired over the range 400–4000 cm^{-1} from 32 co-added scans at 4 cm^{-1} resolution. The resins were sandwiched between two thin polymer films and were tightly attached to the sample holder using small clamps. The polymer was selected because of the absence of overlapping of its characteristic bands with those of BisEMA and pyrrole. The background spectra were collected through an empty polymer assembly. With the assembly in a vertical position, the light source was placed in contact with the polymer film surface. The specimens were irradiated at regular time intervals and spectra were collected immediately after each exposure interval. The conversion of methacrylate groups was calculated from the decay of the absorption band located at 1637 cm^{-1} [24]. The conversion of pyrrole was calculated from the decay of the band at 736 cm^{-1}



Scheme 1. Structure of the photoinitiator and monomers studied.