

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.

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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 poly-methylmethacrylate [13], poly(vinyl alcohol) [14] and poly(vinyl-chloride) 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)phenyliodonium hexafluoroantimonate (Ph_2ISbF_6) (OMAN 071, Gelest Inc., Philadelphia, USA). The free radical photoinitiators 2,2-dimethoxy-2-phenylacetophenone (DMPA), 2-methoxy-2-phenylacetophenone (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.

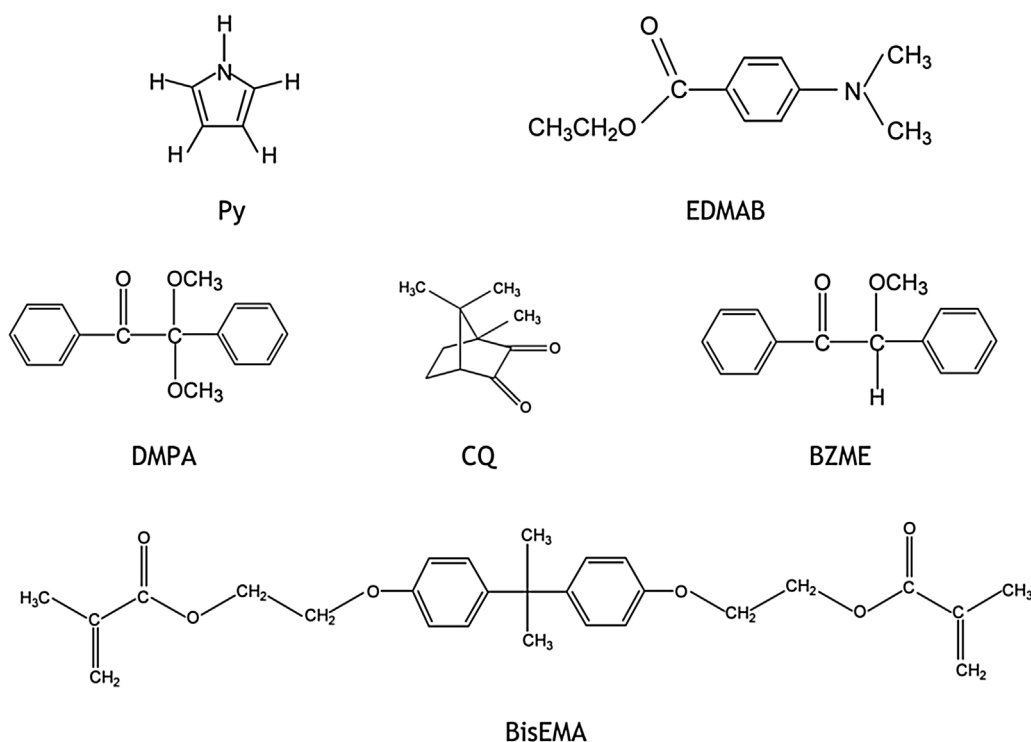
Two light emitting diodes (LEDs) light sources were used in the present study. These LEDs were selected because their spectral irradiances overlap with the absorption spectra of DMPA, BZME and CQ. Mixtures Py/BisEMA containing DMPA and BZME were irradiated with a LED with its emittance centered at 365 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/cm². 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 ± 0.05 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 $400\text{--}4000\text{ cm}^{-1}$ 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.

assigned to C–H out-of-plane bending in the pyrrole ring [25]. In all cases the peak centered at 1510 cm^{-1} was used as internal reference.

For the electrical measurements, silver electrodes were painted on both faces of the sample specimens. Electrical conductivity (σ_d) of mixtures pyrrole/methacrylate was measured by a two-probe method and expressed as the specific volume resistivity ($\Omega\text{ cm}$), employing a Super Megohmmeter Hioki DSM-8104, DSM-8542. The values of electrical conductivity, σ_d were culated from the following equation:

$$\sigma_d = \left(\frac{I}{V}\right) \frac{t}{A} \left(\frac{\text{Siemens}}{m}\right) \quad (1)$$

where t and A are the thickness and area of the specimen, I the current supplied and ΔV is the measured potential drop. Electrical conductivity was also measured in the frequency range 0.10 Hz to 10 MHz, employing both Hioki 3535 and 3522-50 LCR meters.

3. Results and discussion

This section is divided into three parts concerned first with studies of photopolymerization of mixtures pyrrole/methacrylate by UV-vis, followed by measurements of conversion of the individual monomers by FTIR, and finally electrical conductivity characterizations.

3.1. Study of the polymerization of pyrrole by UV-vis spectroscopy

In this section, the photopolymerization of pyrrole (Py) in mixtures pyrrole/methacrylate (Py/BisEMA) containing both radical and cationic photoinitiators is described. Fig. 1 shows pictures of polymerized mixtures BisEMA/Py 97:3 by weight. The mixtures were photoactivated with 1 wt% of DMPA, BZME or CQ/EDMAB either in the absence or the presence of 2 wt% of diaryliodonium salt (Ph_2ISbF_6). Mixtures containing DMPA or BZME were irradiated with a 365-nm LED, while mixtures containing the pair CQ/EDMAB were irradiated at 470-nm. Fig. 1 shows that samples photoactivated with DMPA, BZME or CQ/EDMAB were transparent and colorless indicating that pyrrole did not polymerize in the absence of the diaryliodonium salt. Conversely, samples containing diaryliodonium salt showed a strong brown color associated with

the formation of PPy. From this observation it may be concluded that, under the experimental conditions used in this study, the methacrylate monomer polymerizes by a free radical mechanism photoinitiated by DMPA, BZME or CQ/EDMAB, while pyrrole polymerizes by a cationic mechanism photoinitiated by Ph_2ISbF_6 .

The proposed mechanism of formation of polypyrrole [12] is illustrated in Scheme 2.

The progress of the photopolymerization reaction of pyrrole in mixtures BisEMA/Py 97:3 by weight, photoactivated with different photoinitiator systems, was studied by UV-vis spectroscopy. This technique measures accurately values of absorbance up to 2.5, therefore, only mixtures with low proportion of Py could be analyzed. All samples were irradiated at selected time intervals. Spectra were collected immediately after each exposure interval. The progress of the polymerization was also followed in the absence of radiation. Fig. 2a–c shows the UV-vis spectra of the photopolymerization product recorded at various time intervals. Py, BisEMA, Ph_2ISbF_6 , DMPA and BZME do not absorb in the wavelength range 400–700 nm. Thus, the increase in absorbance with time is attributed to the formation of PPy. It is worth mentioning that the polymerization of Py in the presence of DMPA/ Ph_2ISbF_6 was so fast that a reduced irradiance (75 mW/cm^2) had to be used in order to monitor changes in absorbance during the initial stage of the polymerization. Fig. 2a shows that in the mixture photoactivated with BZME/ Ph_2ISbF_6 as the reaction proceeds two bands develop at 489 and 550 nm. These bands represent the π - π^* transition and bipolaron excitations (Scheme 2), respectively [26–27]. The spectra of the mixture containing DMPA/ Ph_2ISbF_6 in Fig. 2b shows two overlapping bands, the π - π^* transition band at 429 nm and the bipolaron band at about 480 nm. The red-shift of the UV-vis peaks of the mixture photoactivated with BZME/ Ph_2ISbF_6 compared to that photoactivated with DMPA/ Ph_2ISbF_6 is attributed to a comparatively greater size of the oligomers formed in resins containing BZME [26]. The effect of the photoinitiator system on the length of the oligomers will be examined detail later. Fig. 2c shows the UV-vis spectra of the mixture photoactivated with CQ/EDMAB. CQ absorbs in the wavelength range 420–520 nm due to the n,π^* transition of the α -dicarbonyl chromophore, which overlaps with the π - π^* transition associated to the formation of PPy. Moreover, the increase of absorbance during formation of PPy is accompanied with a reduction of absorbance due to the photobleaching of CQ under irradiation at 465 nm [28]. Thus, the photopolymerization of Py with the CQ/EDMAB pair under irradiation at 465 nm is impossible to monitor by UV-vis spectroscopy. On the other hand, the rate of polymerization of Py can be assessed from changes in the UV-vis spectra after the radiation source is switched off. The increase in absorbance in the dark, i.e. in the absence of photobleaching of the CQ, is solely attributed to the formation of PPy.

Fig. 3 compares the increase in absorbance of the π - π^* transition band in resins photoactivated with DMPA and BZME. It is seen that pyrrole polymerizes in the dark because of the living character of cationic polymerization. Results presented in Fig. 3 show that the rate of formation of PPy in mixtures photoactivated with DMPA was markedly faster than that in mixtures containing BZME. Note that mixtures containing DMPA/ Ph_2ISbF_6 were irradiated with a LED of reduced intensity in order to monitor changes in absorbance during the initial stage of the polymerization. Conversely, the polymerization of Py in the mixtures containing CQ/EDMAB (not shown in Fig. 3) was very slow. Fig. 2c shows that the absorbance value changed from 0.45 to 0.65 after 7 h in the dark; i.e., in the absence of photobleaching of CQ. The higher efficiency of DMPA compared with BZME will be explained along with results of conversion monitored by FTIR.

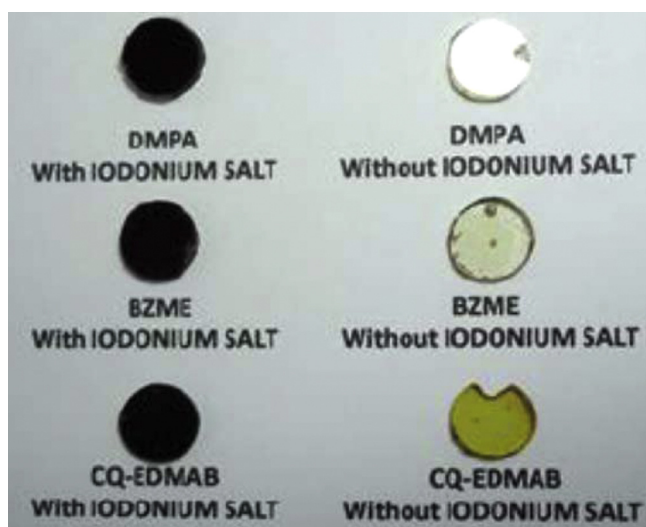


Fig. 1. Pictures showing polymerized samples of mixtures BisEMA/Py 97:3 by weight photoactivated with different photoinitiators systems. The samples were 2 mm thick and 10 mm diameter.

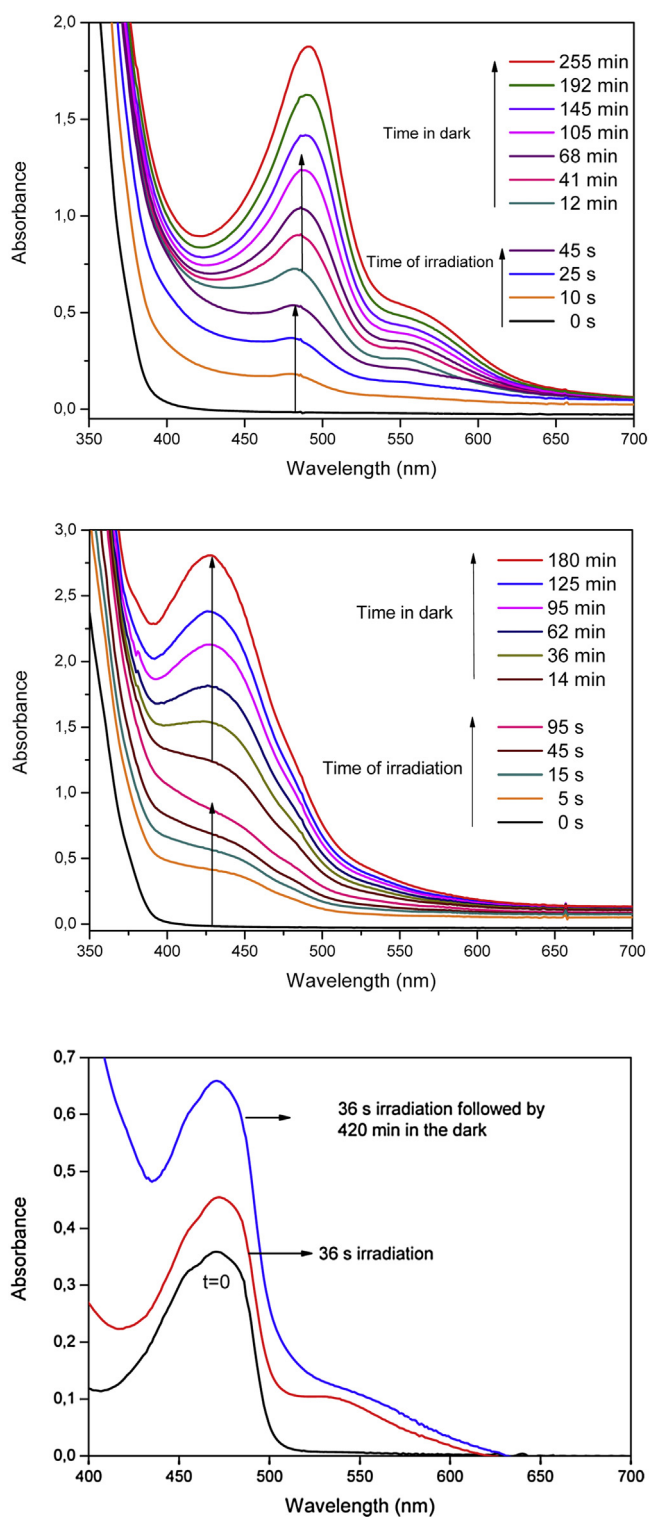


Fig. 2. (a) UV-vis spectra during polymerization of pyrrole in a mixture BisEMA/Py 97:3 by weight photoactivated with 2 wt% Ph_2ISbF_6 in combination with 1 wt% BZME. Samples were irradiated at regular time intervals up to 45 s with a 365 nm LED of 175 mW/cm^2 . After 45 s irradiation the absorbance was monitored at regular time intervals in the absence of irradiation. (b) UV-vis spectra during polymerization of pyrrole in a mixture BisEMA/Py 97:3 by weight photoactivated with 2 wt% Ph_2ISbF_6 in combination with 1 wt% DMPA. Samples were irradiated at regular time intervals up to 95 s with a 365-nm LED of 75 mW/cm^2 . After 95 s irradiation the absorbance was monitored at regular time intervals in the absence of irradiation. (c) UV-vis spectra during polymerization of pyrrole in a mixture BisEMA/Py 97:3 by weight photoactivated with 2 wt% Ph_2ISbF_6 in combination with 1 wt% CQ/EDMAB. Samples were irradiated up to 36 s with a 470-nm LED of 600 mW/cm^2 . After 36 s irradiation the absorbance was monitored in the absence of irradiation. The spectrum at $t=0$ corresponds to the absorbance of the CQ.

matrix. Alternatively, dopants are added into the reaction mixture in order to control the electrical properties of the final polymer [31–32]. The counterion in the system used in this study is the anion of the diaryliodonium salt (SbF_6^-).

Since many years, DMPA and benzoin ether derivatives have been used as UV radical photoinitiators for the polymerization of unsaturated monomers due to their fast photochemical reaction. The different photoinitiation efficiency of DMPA and BZME is attributed to structural effects on the recombination rate of radicals and to the radicals reactivity toward the double bond. Upon irradiation of BZME at 365 nm a Norrish type I cleavage takes place to produce benzoyl (electron withdrawing) and methoxybenzoyl (strong electron donor) primary radicals, as shown in Scheme 3. Similarly, the photolysis of DMPA under irradiation at 365 nm produces dimethoxybenzoyl and benzoyl radicals followed by a fragmentation of the dimethoxybenzoyl radicals to methyl benzoate and methyl radicals (Scheme 3).

Whereas the quantum yield of DMPA consumption in benzene is close to unity [33], the value for BZME is 0.24 [33]. In addition, the molar absorption of DMPA and BZME at 365 nm are 167 and 110 ($\text{l}/\text{mol}\cdot\text{cm}$) respectively. Consequently, it is expected that cleavage of DMPA results in a higher number of reactive radicals compared with BZME. With regard to cationic photopolymerization, it has gained importance after the discovery by Crivello of onium salts as highly photosensitive and efficient cationic photoinitiators [34]. Thermally stable onium salts (On^+) containing aromatic groups such as diaryliodonium ($\text{Ar}_2\text{I}^+\text{X}^-$) or triarylsulfonium ($\text{Ar}_3\text{S}^+\text{X}^-$) salts, with non nucleophilic counter ions such as AsF_6^- , SbF_6^- , BF_4^- , and PF_6^- represent a large class of compounds that can be used as cationic photoinitiators. Upon irradiation with UV light, onium salts decompose to yield a variety of reactive radical, radical-cation and cation intermediates as shown in Eqs. (2)–(4)



The cationic species can interact with a proton donor molecule (RH, i.e. monomer or impurity) giving rise to the strong Brønsted acid, H^+X^- (Eq. (4)) which acts as initiator of cationic polymerization. When photoinitiators such as BZME, DMPA and CQ/EDMAB are irradiated at a wavelength within their absorption range the photochemically generated electron-donating free radicals reduce the iodonium salt [35–38]. This results in the formation of the corresponding carbocations capable of initiating cationic polymerization as illustrated in Scheme 4 [35–38]. In that way, the use of α -cleavage type photoinitiators such BZME and DMPA permits the simultaneous photoinduced polymerization of pyrrole and methacrylate in a one-pot, one-step process. It is worth noting that the higher number of initiating radicals produced during cleavage of DMPA will result in a higher number of polymerizing oligomers having lower molar mass compared with those produced by photolysis of BZME. This explains the red-shift of the UV-vis spectra shown in Fig. 2a and b, which is observed when the size of the oligomers formed increases [26].

Visual examination of the polymers based on Py/BisEMA mixtures showed that phase separation did not occur and the polypyrrole was well dispersed in the methacrylate polymer in the absence of modifiers. From this observation it is concluded that the

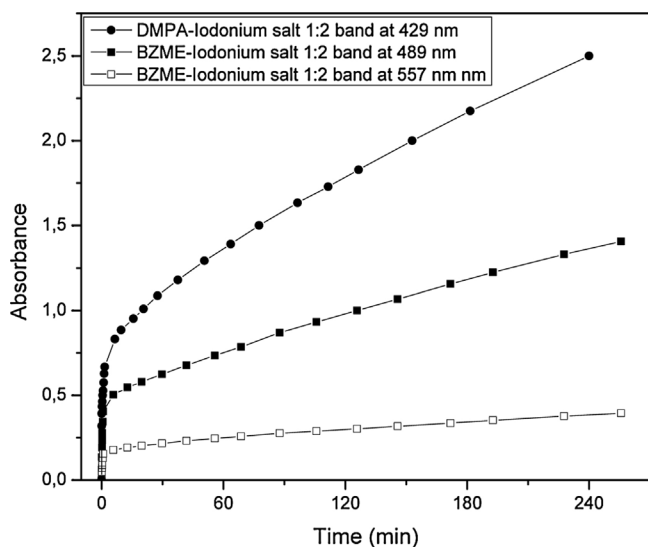


Fig. 3. Absorbance of the π - π^* bands vs time in mixtures BisEMA/Py 97:3 by weight photoactivated with 2 wt% Ph_2ISbF_6 and 1 wt% of either DMPA or BZME. The absorbance of the polaron excitation band in resins containing BZME is also shown. The irradiance in mixtures with DMPA was 75 mW/cm^2 while in mixtures with BZME was 175 mW/cm^2 .

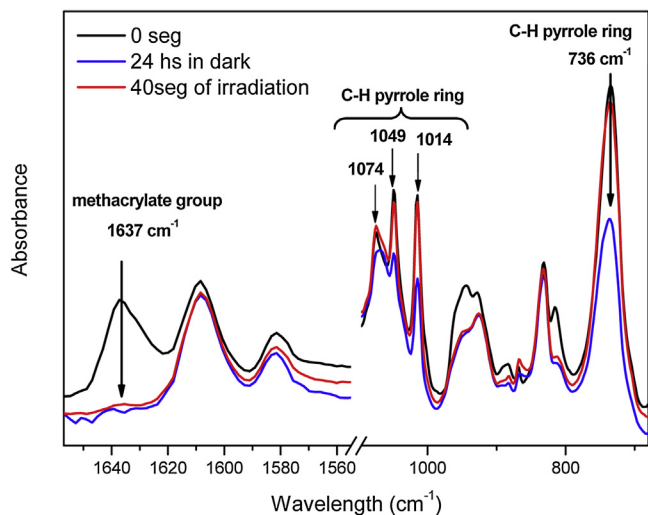


Fig. 4. Characteristic peaks in MIR spectra of a pyrrole/mixture. The band representing the methacrylate double bond is located at 1637 cm^{-1} . The bands at 1074 , 1049 , 1014 and 736 cm^{-1} are assigned to pyrrole.

combination of pyrrole and BisEMA resulted in the formation of interpenetrating polymer networks.

From results of FTIR studies it is concluded that the use of the Ph_2ISbF_6 salt in combination with α -cleavage type photoinitiators such BZME and DMPA permits the simultaneous photoinduced polymerization of pyrrole and methacrylate monomers in a one-pot, one-step process. In that way, 2–3 mm thick layers of interpenetrating networks are obtained.

3.3. Electrical conductivity

Scheme 2 shows that PPy has resonance structures that resemble the aromatic or quinoid forms. In this neutral state PPy is not conducting and only becomes conducting when it is oxidized. The charge associated with the oxidized state is typically delocalized over several pyrrole units and can form a radical cation

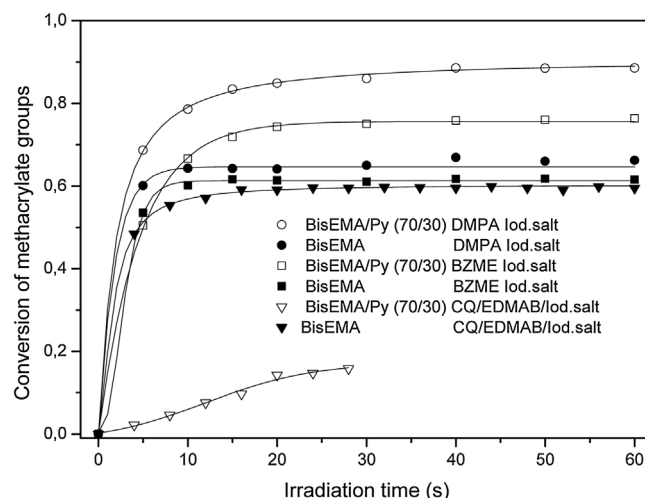


Fig. 5. Conversion of methacrylate groups vs time measured by MIR in mixtures BisEMA/Py 70:30 by weight containing 1 wt% of DMPA, BZME or the CQ/EDMAB pair in combination with 2 wt% Ph_2ISbF_6 (hollow symbols). The conversion of BisEMA pure using the same photoinitiator systems (filled symbols) is shown for comparison.

(polaron) or a dication (bipolaron). The mechanism of conduction in PPy has not been yet conclusively established because of the persistent structural disorder of the polymer. The most widely accepted mechanism involves charge transport along the polymer chains, as well as hopping of carriers (holes, bipolarons, etc.) [6]. A counterion (in this case an anion) stabilizes the charge on the polymer but is not very mobile within the polymer. **Fig. 7** shows the experimental curves I vs V used to calculate the electrical conductivity from Eq (1). The composition of sample specimens used in electrical characterizations and the measured values of electrical conductivity are presented **Table 1**. It is seen a marked increase in conductivity in the system containing 50 wt% Py in combination with 10 wt% Ph_2ISbF_6 and 1 wt% BZME. The observed increase in conductivity is attributed to the formation of a conducting polymer network within the insulating BisEMA matrix. The conversion of Py reached in the mixture containing 50 wt% Py was 0.76 which corresponds to 36 wt% PPy. As described previously, the polymerization of Py is affected by the reduced mobility of the reacting medium as a result of the earlier

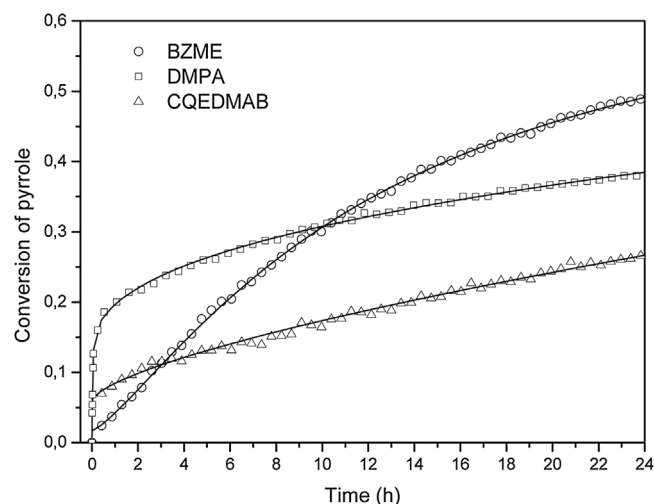
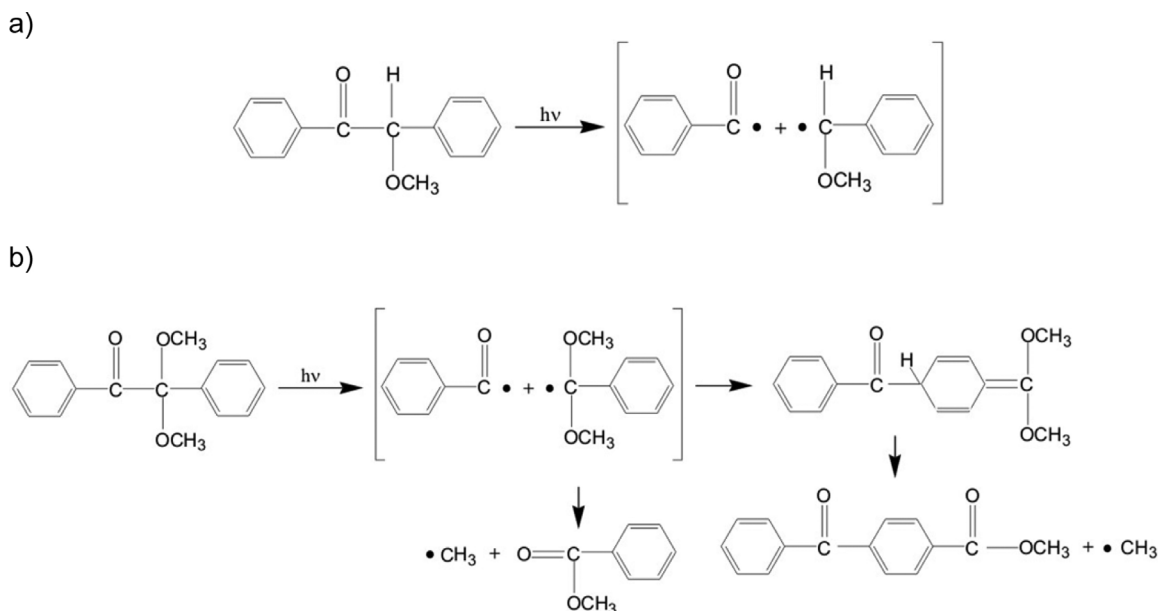
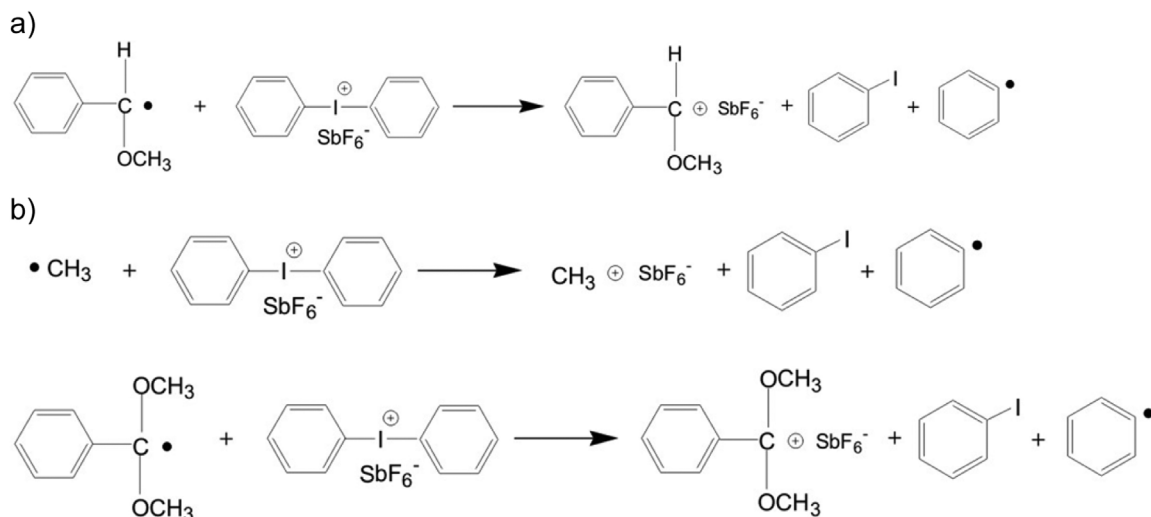


Fig. 6. Conversion of C–H groups of pyrrole vs time measured by MIR in mixtures BisEMA/Py 70:30 by weight containing 1 wt% of DMPA, BZME or the CQ/EDMAB pair in combination with 2 wt% Ph_2ISbF_6 .



Scheme 3. Photolysis of (a) BZME and (b) DMPA under irradiation at 365 nm.



Scheme 4. The photochemically generated electron-donating free radicals derived from (a) BZME and (b) DMPA reduce the iodonium salt to yield the corresponding carbocations capable of initiating cationic polymerization of pyrrole.

vitrification of the methacrylate network. The increased conversion of Py in mixtures Py/BisEMA 50/50 (see Table 1) is explained in terms of an enhancement of the mobility of the reactive species in mixtures with reduced proportions of BisEMA. Unfortunately, systems containing more than 50 wt% Py resulted in brittle polymers having undesired poor mechanical properties. This set a limit in the maximum amount of Py to be added to the BisEMA/Py mixtures.

The electrical conductivity of the BisEMA–PPy composites were also analyzed in the frequency range from 10^2 to 10^7 Hz. The frequency dependent electrical conductivities (σ_a) of BisEMA/PPy formulations containing the proportions of PPy and photoinitiator given in Table 1 are depicted in Fig. 8.

Again, the marked increase in the conductivity of the system containing 50 wt% Py in combination with 10 wt% Ph_2ISbF_6 and 1 wt% BZME is attributed to the comparatively higher amount of conducting PPy in this formulation. It is worth mentioning that the

increase in conductivity in mixtures photoactivated with DMPA was not as marked as that observed in the mixtures prepared with BZME. A probable explanation is that the electronic conductivity is facilitated by the higher size of the oligomers resulting from BZME. It is worth mentioning that the value of σ_a of the system containing 50 wt% PPy in combination with 10 wt% Ph_2ISbF_6 and 1 wt% BZME at 10 MHz is comparable to those reported for composites based on a polyacrylonitrile matrix modified with PPy derivatives [39] and poly *N*-vinylcarbazole– Fe_3O_4 nanocomposites modified with different amounts of PPy [40].

Electrical conductivity studies (Figs. 7 and 8) showed a sudden increase in conductivity at 50 wt% Py. This abrupt increase in conductivity may be explained on the basis of percolation theory, which predicts that at a certain concentration of conducting polymer a full conducting path for the flow of current is formed. It is well known that dispersion of PPy conducting particles in an insulating polymer matrix can impart electrical conductivity when

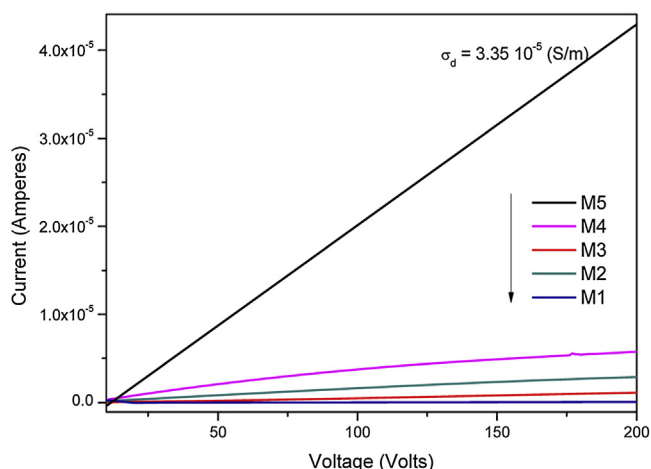


Fig. 7. Current vs voltage in specimens having the proportions of PPy and photoinitiator given in Table 1. The electrical conductivity (σ_d) is calculated from Eq. (1).

Table 1

Composition of sample specimens used in the measurement of electric conductivity. All samples contained 1 wt% BZME. X_{Py} is the conversion of Py measured by ATR after 24 h reaction. The amount of PPy was calculated from conversion values of Py. The electrical conductivity (σ_d) was calculated from Eq. (1).

Sample	Py (wt%)	Ph ₂ ISbF ₆ (wt%)	X_{Py}	PPy (wt%)	σ_d (S/m)
M1	0	–	–	–	1.70×10^{-8}
M2	40	2	0.65	26	2.10×10^{-7}
M3	40	5	0.65	26	1.40×10^{-6}
M4	40	7	0.65	26	4.10×10^{-6}
M5	50	10	0.76	38	3.35×10^{-5}

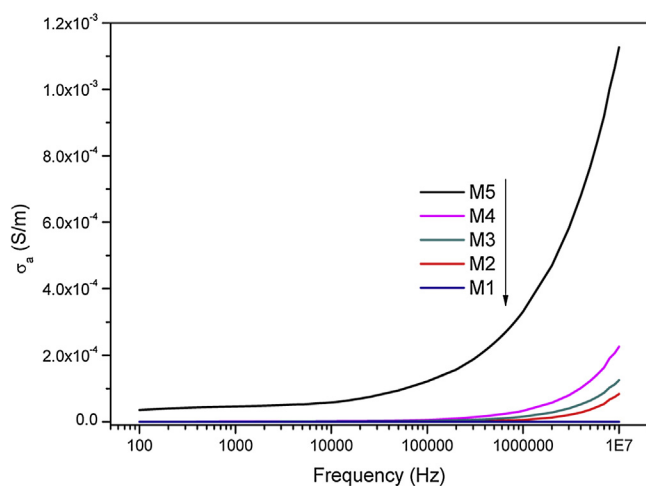


Fig. 8. Variation of electric conductivity (σ_a) with frequency in specimens having the proportions of PPy and photoinitiator given in Table 1.

the particle volume fraction is greater than a value referred to as the percolation threshold [41]. The conductivity of the composite is almost the same as that of the insulating polymer below the percolation threshold because the number of particles is insufficient to form a continuous conducting path. In the vicinity of the percolation threshold, the isolated conductive particles appear to contact each other forming a continuous network for transportation of electrons. Immediately after the percolation threshold, a slight increase in the concentration of conductive particles may greatly increase the bridges in the conducting network [41]. The

insulating composite is thus transformed into a conducting material in a jump wise fashion. Composite materials based on conjugated conducting polymers and non-conducting polymers are another class of conducting polymers that often show a percolation threshold [42–44]. The marked increase in conductivity above the percolation threshold is attributed to the formation of a continuous network of conducting pathways. Then, if the PPy structures are not sufficiently large and numerous to join one another and to build an infinite network, no conduction paths may be established in any direction. The system is then below the percolation threshold, and the PPy film does not conduct electricity.

In conclusion, although mechanistic details still remain to be evaluated, it is clear that Py can efficiently be polymerized in mixtures with methacrylate monomers using a iodonium salt and free radical photoinitiators. The values of electrical conductivity of the resin containing 50 wt% Py in combination with 10 wt% Ph₂ISbF₆ and 1 wt% BZME encourage further research with regard to the incorporation of increasing amounts of Py in alternative photopolymerizable monomers. Further investigations concerning preparation of photocurable mixtures with improved electronic conductivity are now in progress.

4. Conclusions

Mixtures pyrrole/methacrylate photoactivated with an iodonium salt in combination with DMPA or BZME were efficiently polymerized under irradiation at 365-nm. Conversely, in mixtures photoactivated with iodonium salt in combination with the CQ/EDMAB pair irradiated at 470 nm the polymerization of both pyrrole and methacrylate was very slow.

Microscopy studies revealed the absence of phase separation indicating that the combination of pyrrole/methacrylate resulted in the formation of an interpenetrating polymer network.

The electrical conductivity of the hybrid polymers was markedly affected by the amount of PPy present in the formulations.

Up to 50 wt% Py and 10 wt% iodonium salt could be incorporated into the mixtures without jeopardizing the mechanical integrity of the sample specimens.

Acknowledgements

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