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The efficiency of photoinitiators in ionic liquids

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ABSTRACT

In this work, efficiency of initiation of the photopolymerization in ionic liquids (ILs) by four Type I photoinitiators (PIs) was investigated. The influence of the ILs on the initiation process was determined by investigation of the polymerization kinetics and by spectroscopic and photolysis studies. The polymerization initiated by three of the tested PIs proceeded faster in ionic liquids, whereas the efficiency of the photoinitiator depended strongly on the structure of the ionic liquid. In one case, (2-methyl-4′-(methylthio)-2-morpholinopropiophenone), there was a significant reduction in the reaction rate, which resulted from a drastic decrease in the quantum yield of photolysis of this photoinitiator in ionic liquids. The results obtained suggest that for every composition containing an ionic liquid, the photoinitiator should be matched individually.

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1. Introduction

During the last years a great interest has been shown for polymerization conducted in ionic liquids (ILs). The first reason advanced for this development is usually the need for "green solvents" to replace volatile organic compounds (VOCs) [1]. But studies have shown that this is not the only reason for the development of polymerization in ILs. In fact, most of the polymerizations carried out in ILs show an increase in the polymerization rate and in the polymer chain length compared to polymerization in classical organic solvents [2–7]. The increase in the polymerization rate in the presence of ILs was ascribed both to the enhancement of the propagation rate coefficient (k_p) due to dipolarity/polarizability effects [8] associated with a decrease in the activation energy of propagation [4–7] as well as to the reduction of the termination rate coefficient (k_t^b) due to the increase in system viscosity after IL addition [5,6,9,10]. These effects led to an increase in k_p and decrease of k_t^b with the increasing IL concentration. In some cases the polydispersity index of the final polymer was decreased [11,12] and linear block polymers have been obtained for a radical initiation [13,14].

Ionic liquids can also act as plasticizers, stabilizers, modifiers, etc. [1] and gel polymer electrolytes can be produced by thermal polymerization of monomers in ILs leading to the formation of composite conducting materials [15–18]. This latest application has also been studied using a photoinduced polymerization and membranes [19] and solid polymer electrolytes have been obtained [20–24].

Photopolymerizations present some advantages compared to thermal induced polymerizations, such as a short reaction time and a spatial and temporal control of the reaction [25,26]. In addition, formulations used in photopolymerization do not contain VOCs and are therefore very attractive from the industrial point of view. Only the initiation is different from a thermal polymerization: the penetration of light in the sample is required to create the active species (radicals or cations). However, despite numerous and extensive studies on the polymerization reaction in ionic liquids, only few papers dealt with a photoinitiated polymerization [9,21,22,27–39]. Some of these works [9,28,29] focused on the photopolymerization of ionic liquids bearing monomer functions in order to get structured materials. Generally, the popular commercial Type I photoinitators (photofragmenting), like 2,2-dimethoxy-2-phenylacetophenone (DMPA) [9,21,24,27,33], 1-hydroxycyclohexyl-acetophenone [32,39] or 2-hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-1-propanone were used to initiate the photopolymerization in ILs [9,33]. Only one research group used a type II photoinitator (H-abstracting) – phenantrene quinone [30,36].

Most often the photopolymerization processes are carried out in bulk and efficiencies of photoinitiators are referred to such conditions. On the other hand, investigation of photophysical processes and studies of the photochemical reactivity are mainly carried out in molecular (non-ionic) solvents. In both cases the properties of the

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Table 1
Viscosities of the monomer, diluent/monomer mixtures and diluents at 20 °C.

	Formulation viscosity, mPa s Diluent content, wt.%				
	0	30	50	70	100
[EMIm][BF$_4$]		110.63	131	117.07	54
[BMIm][BF$_4$]	49.66	126.02	149.9	148.4	131.6
[EMIm][OTf]		96.96	96.98	86.6	45
TCP		56.58	62.6	68.5	75.5

reaction medium are far different from those in ILs. Due to complexity of reactions occurring during the photodissociation, it is possible that ILs influence these reactions.

Until now the initiation step in ILs was investigated only for the above mentioned Type II photoinitiator, phenantrene quinone, and no influence of ILs on the photoreduction kinetics was found [30,36]. However, no research has been made concerning the influence of ILs on the effectiveness of Type I photoinitiators. Taking into account the advantages of the UV-induced polymerization in ILs and its practical applicability, e.g. for preparation of solid polymer electrolytes [20–24,31], it was of interest to check the initiating efficiency of several popular commercially available photoinitiators producing radicals by direct photolysis of a week bond. An additional motivation was the fact that type I photoinitators are used in determination of the polymerization rate coefficients by the PLP-SEC technique, recently also in ILs (2-methyl-4′-(methylthio)-2-morpholinopropiophenone [8,10,40,41], benzoin [5], DMPA [7]).

The results reported here concern (i) the effect of the PI structure on its activity in the initiation of polymerization in ILs and (ii) the behaviour of PIs during their photolysis in ILs. Additionally, other effects which can affect the initiating effectiveness are discussed. The investigations were performed for four Type I photoinitators and three imidazolium-based ILs.

2. Materials and methods

2.1. Materials

The photoinitiators: Irgacure 907 (2-methyl-1-(4-methylthio)phenyl-2-morpholinyl-1-propanone (synonym: 2-methyl-4′-(methylthio)-2-morpholinopropiophenone), Irg 907), Irgacure 184 (1-hydroxycyclohexyl-acetophenone, Irg 184) and Irgacure 819 (phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, Irg 819) have been provided by Ciba Sp. and used as received. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) was purchased from Aldrich and used without further purification.

Polyethyleneglycol dimethacrylate PEGDMA (M_n ~550 g/mol, Aldrich) was purified on an aluminium oxide column before use. Tricresylphosphate (TCP, mixture of isomers, 90%) was purchased from Aldrich and used as received.

1-Ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIm][OTf]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF$_4$]), and 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm][BF$_4$]) were purchased from Merck and were of high purity ($\geq$99.0%; water content $\leq$100 ppm; halide content $\leq$100 ppm, High Quality).

2.2. Polymerization kinetics

Reaction rate (R_p) profiles and conversions (p) were determined by differential scanning calorimetry (DSC) under isothermal conditions (20 °C) using a Pyris 6 instrument (Perkin-Elmer). It was equipped with a lid especially designed for photochemical measurements. The DSC instrument was calibrated with a standard Indium sample of known mass, melting point temperature, and known associated enthalpy change. The 2 mg samples were polymerized in open aluminium pans having a diameter of 6.6 mm. The DSC chamber was purged with argon of high purity (<0.0005% of O_2) for 10 min prior to irradiation in order to remove oxygen from the chamber and that dissolved in the sample. The polymerizations were initiated by the light from a Hg/Xe lamp (Hamamatsu, band pass filter centred around 366 nm, total light intensity 0.3 mW/cm^2) 5 s after the beginning of the measurement. All the DSC photopolymerization experiments were conducted in triplicate. The reproducibility of the results was about ±6% leading to an uncertainty on the R_p value around ±0.0006 for most of the samples. For computations, the heat of polymerization was taken to be 56 kJ/mol per double bond [42].

2.3. Diffusion rate coefficients

Diffusion rate coefficients, k_{diff}, were calculated from the well-known relation [27,43]

$$k_{\text{diff}} = \frac{8000 \cdot R \cdot T}{3 \cdot \eta} \tag{1}$$

where k_{diff} is expressed in [dm^3 mol^{-1} s^{-1}], R is gas constant [J mol^{-1} K^{-1}], T is temperature [K], and η is system viscosity [Pa s].

Viscosity (η) measurements have been performed on a Brookfield Digital Viscometer (DV-II) at 20 °C (polymerization temperature). The η values were found to be shear rate independent. Viscosities of the monomer, diluents and monomer/diluent mixtures are given in Table 1.

It is worth noting that the monomer/IL mixtures show a viscosity synergism, which has been reported earlier by us in Ref. [27].

2.4. UV–visible spectroscopy

UV–visible spectra were recorded on a Cary 4000 (Varian) spectrophotometer in a 1 mm optical pathway quartz cell. The molar extinction coefficients were calculated using the Beer–Lambert equation: $OD = \varepsilon \ell C$ with OD the optical density of the solution at a given wavelength, ℓ is the optical pathway of the cell and C is the photoinitiator concentration.

2.5. Photolysis

The photolysis of the photoinitiators was performed in acetonitrile, benzene and [BMIm][BF$_4$] using an Oriel Hg-lamp (200 W) with a 314 nm or 366 nm interferential filter for the irradiation. The evolution of the UV–visible spectrum (bleaching of the photoinitiator most of the time) was recorded as a function of the irradiation time on a Cary 4000 spectrophotometer in a 1 cm optical pathway quartz cell. The photoinitiator solution was stirred continuously during the irradiation and was purged with argon to avoid the oxygen inhibition. Phenylglyoxalic acid in acetonitrile/water (3:1) solution was used as a chemical actinometer [44]. The initial optical density of the sample solution and the one of the actinometer solution at the irradiation wavelength were similar in all the experiments. The photolysis quantum yields were then calculated from

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