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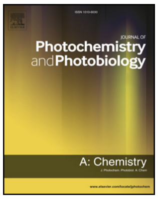

Regulating photochemical behavior and property of imidazolium-based water soluble polysiloxane macromolecular photoinitiators by anions

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ABSTRACT

Five polysiloxane macromolecular photoinitiators containing different anion structures with ionic liquid character ([Si-di2959Im][X] (X = Br^-, Ph_4B^-, TsO^-, NO_3^-, CF_3COO^-)) were designed and synthesized. The effect of different anion structures on photochemical behavior, phoinitiating mechanism, the water solubility, thermal property and volatility of the photoinitiators was systematically explored. [Si-di2959Im][X] have high extinction coefficient that reaches up to 40,210 M^{-1} cm^{-1}, and similar photoinitiating activity and mechanism to 2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methylpropan-1-one (Irgacure 2959), while the photopolymerization induction periods of the TPGDA systems initiated by [Si-di2959Im][X] (X = Ph_4B^-, CF_3COO- and NO_3) are slightly shorter than that by Irgacure 2959. In addition, [Si-di2959Im][X] have not only good water solubility, but also desirable thermal property and low saturated vapor pressure. The order of water-solubility of [Si-di2959Im][X] is $Ph_4B^- < Br^- < TsO^- < NO_3^- < CF_3COO^-$, the order of the saturated vapor pressure is $CF_3COO^- < Ph_4B^- < NO_3^- < Br^- < TsO^-$. High-performance liquid chromatography chromatograms reveal that the migration of the photolysis fragments of [Si-di2959Im][X] from the cured material is mitigated significantly by their high molecular weights.

1. Introduction

Photoinitiated polymerizations have been employed in free radical [1,2], cationic [3,4], and in rare cases, anionic [5] polymerization systems. Free radical and cationic photopolymerization reactions have been greatly utilized in various conventional and emerging applications, such as coatings, electronic circuits, digital storage and 3D precision machining. But the cationic photopolymerization has its limitations in cost and curing speed and so on. Compared with traditional free radical photopolymerization technology, water–based photopolymerization technology exhibits not only significant advantages in fast polymerization rate and low polymerization temperature, but also environmental-friendly characteristics because water replaces harmful monomers as diluents [6–10]. The water-soluble photoinitiators play a pivotal role in water–based UV curable systems. They can absorb the light energy of appropriate wavelength and then produce primary radical species to initiate polymerization. Low molecular weight photoinitiators, however, have many intrinsic disadvantages such as odor, toxicity, poor water solubility and darkening due to the presence of migratory residues in the cured films [11,12]. Therefore, to design and synthesize a photoinitiator with good water solubility, and low volatility and migration has been the research focus in the field of water-based photopolymerization recently. Generally, water-soluble photoinitiators can be developed by grafting hydrophilic groups such as quaternary ammonium salts, sulfonates, and carboxylic acid groups [13–15], which usually lead to relatively poor thermal stability or low photoinitiation efficiency. Ionic liquids (ILs), a class of unique substances composed purely by cations and anions, are renowned for their fascinating physical and chemical properties [16,17]. In particular, some of their unique chemical and physical properties show potential applications for the preparation of photoinitiators with good water solubility such as the excellent solubility, low toxicity, thermal stability and low volatility. The anion of ionic liquid is a key factor that affects the performance of the photoinitiator, including photochemical performances and phoinitiating mechanism, and physical properties of the photoinitiator. Furthermore, polysiloxanes possess some wonderful features involving excellent chemical/thermal stability and surface property [18,19]. They stimulate our interest to fabricate a hydrophilic imidazolium-based polysiloxane macromolecular photoinitiator with different anion groups, which has new satisfying properties including

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excellent water–solubility and thermal stability, and low volatility and migration for water-based UV-curable systems.

In this article we have designed and synthesized five bifunctional imidazolium polysiloxane macromolecular photoinitiators containing different anions ([Si-di2959Im][X] (X = Br^-, Ph_4B^-, TsO^-, NO_3^-, CF_3COO^-)) based on imidazolium, 2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl propan-1-one (Irgacure 2959) and polysiloxane. The effect of anions on photoinitiating behaviors, and photodegradation and photoinitiation mechanism of the photoinitiators was systematically investigated through UV absorption spectroscopy, real-time infrared (RTIR) spectroscopy and electron spin resonance (ESR). The solubility of [Si-di2959Im][X] (X = Br^-, Ph_4B^-, TsO^-, NO_3^-, CF_3COO^-) in aqueous solution was tested. The thermal properties and volatility of [Si-di2959Im][X] (X = Br^-, Ph_4B^-, TsO^-, NO_3^-, CF_3COO^-) were examined using thermogravimetric analysis (TGA). The migration of photolysis fragments of the photoinitiating groups from the photopolymerization materials was also investigated through high–performance liquid chromatography (HPLC-MS). Besides, the physical and mechanical properties of cured films initiated by [Si-di2959Im][CF_3COO] were also evaluated.

2. Experimental section

2.1. Material and characterization

Methylene chloride (CH_2Cl_2), tetrahydrofuran (THF), anhydrous sodium sulfate (Na_2SO_4), potassium hydroxide (KOH), 2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methylpropan-1-one (Irgacure 2959), 4-toluene sulfonyl chloride, imidazole, acetonitrile, sodium hydride, silver nitrate, silver trifluoroacetate, sodium tetraphenylborate, petroleum ether, ethanol and ethyl acetate were purchased from Sinopharm Group Chemical Reagent Co. (Beijing, China). Alkylhydroxyl polysiloxane (HO—Si—OH) (Mn = 910) was a gift from Shin-Etsu Chemical Co. Ltd (Shanghai, China). Tripropylene glycol diacrylate (TPGDA) and acrylamide (AM) were purchased from Eternal Chemical Co. Ltd. (Tianjin, China). 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was supplied by Shanghai Chemical Reagents Co. (Shanghai, China). All reagents were used as received without further purification.

^{1}H-NMR spectra were recorded using an AV400 unity spectrometer (Bruker, USA) operated at 400 MHz with $CDCl_3$ as a solvent and tetramethylsilane as an internal standard.

FTIR spectra were recorded by using a Nicolet 50XC spectrometer (Nicolet, USA) and scanned between 400 and 4000 cm^{-1}.

The properties of UV absorption and UV degradation were studied by UV/vis spectroscopy (Hitachi High-Technologies Corporation, Tokyo, Japan).

ESR experiments were carried out using an X-band spectrometer (JES-FA200 JEOL Ltd) at 9.06 GHz employing 100 kHz field modulation and a microwave power of 0.998 mW. The radicals were generated at room temperature upon the high pressure mercury lamp exposure under an argon protection and trapped by DMPO. The photoinitiator and DMPO were added into methylene chloride to obtain a solution with the concentration of 1×10^{-4} mol L^{-1}, and then the solution was irradiated. The molar ratio of the photoinitiator to DMPO was 1:5. The ESR spectra simulation was carried out using the MATLAB software.

The thermal properties of [Si-di2959Im][X] and UV-cured films prepared using [Si-di2959Im][X] were determined by STA-449C simultaneous thermal analyzer (Netzsch, Germany). Samples were run from 30 to 600 °C with a heating rate of 10 °C min^{-1}.

The HPLC–MS analysis was performed on an Agilent 1100 series instrument coupled to a MS detector. Samples were separated on a C_{18} column (5 u m, 150 × 4.6 mm i.d.) with a sample injection volume of 25 μL. The mobile phase was mixtures of acetonitrile (A) and water (B). A gradient program was used as follows: 70% A (0 min), 70% A (2 min), 100% A (5 min). The mobile phase flow rate was 1.0 mL min^{-1}.

Photopolymerization kinetics was investigated by real-time infrared (RTIR) spectroscopy equipped with an MCT/A detector and an extended range KBr beam splitter (Nicolet 5700, Thermo Electron, USA) [20].

Dynamical thermal mechanical analysis (DMTA) was performed on DMTA-IV (Rheometric Scientific Co.) to measure glass transition temperature (Tg) of cured films. Measurements were collected from -50 to 200 °C with a heating rate of 5 °C min^{-1}, at a frequency of 1 Hz.

The tensile properties of cured films were measured using a material testing instrument (Instron-1211, USA) at 25 °C. The rate of extension was 10 mm min^{-1}.

Pencil hardness apparatus AR015 (Tianjing Instrument Co., China) was employed to measure the hardness of cured films.

2.2. Synthesis of [Si-di2959Im][Br] and [Si-di2959Im][TsO]

First, polysiloxane modified imidazole derivatives (**Im-Si-Im**) was prepared through a two-step procedure (the synthesis routes are shown in Scheme 3 and detailed descriptions are shown in Supporting information). Then, two small-molecular photoinitiators (**Br-2959** and **TsO-2959**) were synthesized by a known procedure [21,22]. Finally, **Im-Si-Im** reacted with **Br-2959** and **TsO-2959** respectively to obtain two imidazolium-based water soluble polysiloxane macromolecular photoinitiators ([Si-di2959Im][Br] and [Si-di2959Im][TsO]). The photoinitiators containing anions of Ph_4B^-, TsO^-, NO_3^- and CF_3COO^- were prepared by anion exchange reaction, and detailed description is as follows.

In a three-neck round-bottom flask equipped with a condenser and a magnetic stirrer, **Im-Si-Im** (2 mmol) and **Br-2959** (1.37 g, 4.8 mmol) or **TsO-2959** (1.75 g, 4.8 mmol) were dissolved in anhydrous acetonitrile (5 mL) under N_2 atmosphere. The reaction was performed under stirring at 80 °C for 48 h. Then, the solvent was removed by vacuum distillation. The crude product was washed three times with diethyl ether. After filtration, the final product was dried in a vacuum drying oven at 40 °C for 24 h. The yield was 90.2% and 91.5%, respectively. The synthesis process is shown in Scheme 1.

[Si-di2959Im][Br]: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.29 (s, 2H, CH), 8.21 (d, J = 8.8 Hz, 4H, ArH), 7.84 (d, J = 40.0 Hz, 4H, CH), 7.02 (d, J = 8.7 Hz, 4H, ArH), 4.67 (t, J = 5.0 Hz, 4H, CH_2), 4.46 (t, J = 4.9 Hz, 4H, CH_2), 4.39 (t, J = 4.9 Hz, 4H, CH_2), 3.73 (t, J = 4.9 Hz, 4H, CH_2), 3.47 (t, J = 5.0 Hz, 4H, CH_2), 3.18 (s, 2H, OH), 1.50–1.42 (m, 4H, CH_2), 1.38 (s, 12H, CH_3), 0.42–0.64 (m, 4H, CH_2), 0.15 – 0.03 (m, 60H, CH_3). FTIR (KBr, cm^{-1}): 2923 cm^{-1}, 2870 cm^{-1} ($-CH_3$, $-CH_2$), 1724 cm^{-1}, 1681 cm^{-1} ($> C{=}O$), 1600 cm^{-1} ($-CH{=}CH-$), 1179 cm^{-1} (C—O—C), 1034 cm^{-1} (Si—O—Si), and 799 cm^{-1} (Si—CH_3). ^{29}Si-NMR (80 MHz, DMSO, ppm): δ 9.92 ($-CH_2Si(CH_3)_2$–O–), −21.97 (–Si$(CH_3)_2$–O–).

[Si-di2959Im][TsO]: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.26 (s, 2H, CH), 8.21 (d, J = 9.0 Hz, 4H, ArH), 7.87 (d, J = 2.0 Hz, 2H, CH), 7.77 (d, J = 1.8 Hz, 2H, CH), 7.49 (d, J = 8.0 Hz, 4H, ArH), 7.12 (d, J = 7.8 Hz, 4H, ArH), 7.01 (d, J = 9.0 Hz, 4H, ArH), 4.65 (t, J = 4.8 Hz, 4H, CH_2), 4.45 (t, J = 4.9 Hz, 4H, CH_2), 4.38 (t, J = 5.0 Hz, 4H, CH_2), 3.72 (t, J = 5.0 Hz, 4H, CH_2), 3.33 (d, J = 6.4 Hz, 4H, CH_3), 2.29 (s, 6H, CH_3), 1.53–1.41 (m, 4H, CH_2), 1.39 (s, 12H, CH_3), 0.49–0.35 (m, 4H, CH_2), 0.14–−0.03 (m, 60H, CH_3). FTIR (KBr, cm^{-1}): 3086 cm^{-1} (Ar–H), 2923 cm^{-1}, 2870 cm^{-1} ($-CH_3$, $-CH_2$), 1724 cm^{-1}, 1681 cm^{-1} ($> C{=}O$), 1600 cm^{-1} ($-CH{=}CH-$), 1179 cm^{-1} (C—O—C), 1034 cm^{-1} (Si—O—Si), and 799 cm^{-1} (Si—CH_3). ^{29}Si-NMR (80 MHz, DMSO, ppm): δ 9.92 ($-CH_2Si(CH_3)_2$–O–), −21.97 (–Si$(CH_3)_2$–O–).

2.3. Synthesis of [Si-di2959Im][NO_3] and [Si-di2959Im][CF_3COO]

The compound [Si-di2959Im][Br] (1 mmol) was dissolved in water to obtain a clear solution. Then, the solution of silver nitrate or silver trifluoroacetate (2 mmol) was added, followed by stirring at room temperature for 48 h. The reaction mixture was filtered through celite to remove solid metal halide. The solvent was removed under reduced