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Polymer 48 (2007) 2199–2202
polymer
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Polymer Communication

Photochemically initiated free radical promoted living cationic polymerization of isobutyl vinyl ether

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Received 24 January 2007; received in revised form 15 February 2007; accepted 16 February 2007
Available online 22 February 2007

Abstract

A new photoinitiating system for living cationic polymerization of vinyl ethers such as isobutyl vinyl ether (IBVE) has been reported. The photoinitiating system comprises free radical photoinitiators such as 2,2-dimethoxy-2-phenyl acetophenone (DMPA), benzophenone or thioxanthone, together with an onium salt, such as diphenyliodonium chloride and zinc bromide. In the first step, photochemically generated free radicals are oxidized to the corresponding carbocations which subsequently react with vinyl ether monomer to yield an adduct. In the presence of zinc salt, this adduct initiates living cationic polymerization of IBVE.

Keywords: Photopolymerization; Living cationic polymerization; Electron transfer

1. Introduction

The discovery of the living cationic polymerization of vinyl ethers, dienes and styrenes furnished a precious tool in the synthesis of well-defined macromolecules with number of functional groups, molecular weight, and polydispersity [1]. A key to the success of the living cationic polymerization is the stabilization of the unstable carbocations via suitable nucleophilic counter anion originating from the initiator and the catalyst. Generally, protonic acids like hydrogen iodide are employed as the initiators, while Lewis acids like zinc iodide are employed as the catalysts [2–5].

Recently, photoinduced living cationic polymerization of isobutyl vinyl ether (IBVE) in the presence of various diphenyliodonium salts and zinc halides was reported by Mah and coworkers [6,7]. Photochemically generated protonic acid reacts with IBVE to form monomer HX-adduct. Terminal carbon–halide bond in this adduct is activated by the coordinating effect of zinc halide. This activation leads to generation of suitable nucleophilic counter anion by stabilizing the growing carbocation. Thus, chain breaking processes are prevented and living cationic polymerization of IBVE proceeds (Scheme 1).

The spectral response of simple diphenyliodonium salts is usually below 300 nm and for their practical application it is often required to extend it to longer wavelengths. Several attempts have been described to overcome this problem in classical photoinduced cationic polymerization. These include electron transfer reactions either with photoexcited sensitizers (i) [8–17], free radicals (ii) [18–20], or electron donor compounds in the excited charge transfer complexes (iii) [21,22].

This paper describes photochemically initiated free radical promoted living cationic polymerization of IBVE by using free radical photoinitiators, such as 2,2-dimethoxy-2-phenyl acetophenone (DMPA), benzophenone and thioxanthone in the presence of iodonium and zinc halides.

2. Experimental

2.1. Materials

Isobutyl vinyl ether (IBVE) and solvents were purified by conventional drying and distillation procedures. Benzophenone (Merck) was recrystallized from heptane. Thioxanthone (Fluka)

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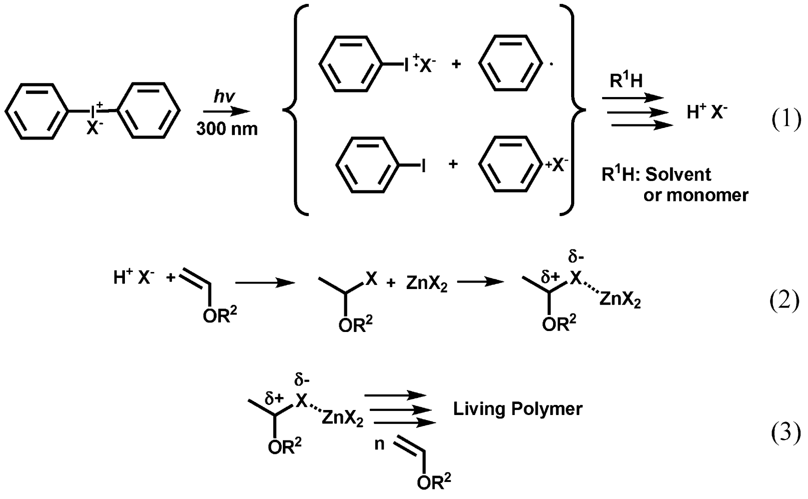
doi:10.1016/j.polymer.2007.02.048



Scheme 1.

was recrystallized from hexane. Zinc bromide ($ZnBr_2$, Aldrich), 2,2-dimethoxy-2-phenyl acetophenone (DMPA, Ciba Specialty Chemicals), and diphenyliodonium chloride (DPICl, Fluka) were used as received.

2.2. Photopolymerization

Monomer (IBVE, $0.38\ \mathrm{mol\ L^{-1}}$) solution in CH_2Cl_2 (2 mL), initiator (DPICl, $2.45 \times 10^{-3}\ \mathrm{mol\ L^{-1}}$), photosensitizer (DMPA, $2.45 \times 10^{-3}\ \mathrm{mol\ L^{-1}}$), and catalyst ($ZnBr_2$, $3.15 \times 10^{-3}\ \mathrm{mol\ L^{-1}}$) were put into a Pyrex tube that was heated *in vacuo* with a heat gun and flushed with dry nitrogen. Almost homogenous mixture was irradiated at −5 °C in a photoreactor (Rayonet) equipped with 16 lamps emitting light nominally at 350 nm. The light intensity was $1.04 \times 10^{-3}\ \mathrm{mW\ cm^{-2}}$ as measured by Delta Ohm model HD-9021 radiometer. After 1 h, the mixture was allowed to stand in the dark at −5 °C for a given time. The resulted polymers were precipitated in the ammoniacal methanol. After precipitation, the polymer was washed with 10% aqueous sodium thiosulfate solution and distilled water, and then dried under reduced pressure. Conversion of monomer was determined gravimetrically. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) consisting of a Waters 410 Differential Refractometer detector, a Waters 515 HPLC pump, and Waters Styragel columns (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0.3 mL/min.

3. Results and discussion

The discovery of the living cationic polymerization (LCP) of vinyl ethers provided a valuable new tool in the synthesis of materials with novel architectures [23]. However, the corresponding photoinitiated polymerization has only been scarcely investigated [6,7]. As stated in Section 1, the only report that concerns the photochemical generation of the protonic acids from onium salts with nucleophilic counter anions. This way, the problems associated with handling of gaseous protonic acid required in the classical living cationic polymerization procedure for the preparation of monomer acid adduct are avoided. The decomposition of onium salts was achieved around 300 nm as related to their absorption characteristics. This brings some limitations on the potential uses of cationic polymerization particularly when long wavelength light sources are used [24,25]. Moreover, weak absorbance of the components of the initiating system may interfere with that of the iodonium salt. Therefore, it seemed appropriate to employ indirect photoinitiating systems to overcome such limitations. Among the indirectly acting initiating systems described for photoinitiated curing applications, free radical promoted cationic polymerization is the most flexible route, since free radical photoinitiators with a wide range of absorption characteristics are available. Many photochemically formed radicals [26–35] can be oxidized by onium salts. In free radical promoted living cationic polymerization, DMPA was used as a radical source. When irradiated in the presence of onium salts such as diphenyliodonium chloride at 350 nm where the onium salt is transparent, the light is absorbed only by DMPA (Fig. 1).

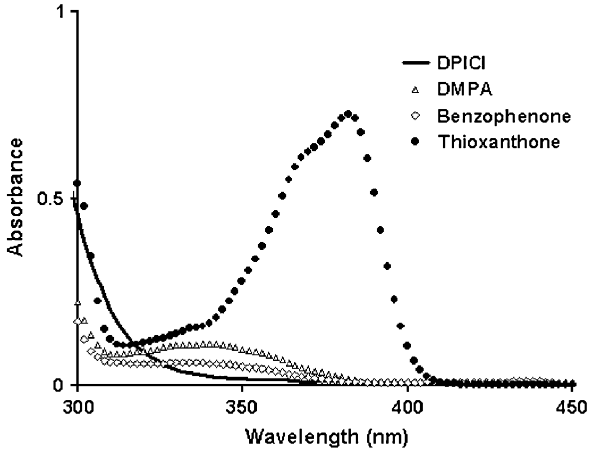
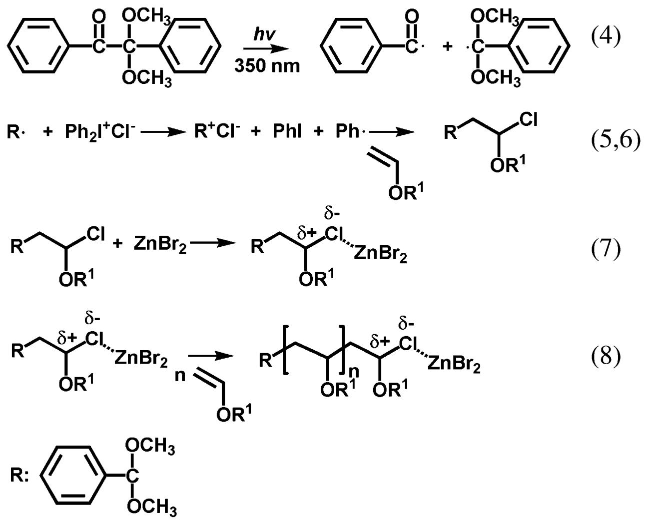


Fig. 1. UV spectra of the solutions of the photoinitiators and diphenyliodonium chloride in CH_2Cl_2. The concentration of solutions was $3.5 \times 10^{-4}\ \mathrm{mol\ L^{-1}}$ in all cases.



Scheme 2.

The photolysis of DMPA results in α-cleavage, and alkoxybenzyl and benzoyl radicals were formed. The strong electron donor alkoxybenzyl radicals thus formed were oxidized by iodonium salt to yield corresponding carbocations which form adducts with the monomer. Subsequent polarization of C-halide terminal of the adduct by the coordination action of zinc bromide facilitates insertion of weakly basic monomer. It should be pointed out that the iodonium salt with nucleophilic chloride counter anion was deliberately chosen to allow the formation of the monomer adduct in the initial step. Non-nucleophilic counter anions such as PF_6^-, SbF_6^-, *etc.* would have caused fast but uncontrolled chain growth as observed in conventional photoinitiated cationic polymerization of vinyl ethers. The overall process is presented in Scheme 2.

Table 1
Photoinitiated free radical promoted living cationic polymerization[a] of IBVE in the presence of DPICl with zinc bromide by using various free radical photoinitiators at −5 °C in CH_2Cl_2 at $\lambda = 350$ nm

System	Photosensitizer	Conversion (%)	Polydispersity[b]	M_n[b]
Direct[c]	–	21	1.20	8500
Indirect	DMPA	18	1.58	17,200
Indirect	Thioxanthone	56	1.57	127,700
Indirect	Benzophenone	63	1.65	141,800

[a] $[IBVE] = 3.84$ mol L^{-1}, $[DPICl] = 2.45 \times 10^{-3}$ mol L^{-1}, $[sensitizer] = 2.45 \times 10^{-3}$ mol L^{-1}, and $[ZnBr_2] = 3.15 \times 10^{-3}$ mol L^{-1}; irradiation time = 1 h; total polymerization time = 20 h.

[b] Estimated by GPC based on polystyrene standards.

[c] Photopolymerization carried out at 300 nm.

In principle, it is not matter whether the initiating free radicals are obtained via α-cleavage or hydrogen abstraction mechanisms. Both types of radical sources have been utilized in order to support mechanistic ideas. Representative results are given in Table 1. It is interesting to note the higher activity of the hydrogen abstraction type photoinitiators, namely benzophenone and thioxanthone which absorb the light between 350 and 450 nm in their ground states (see Fig. 1). In these cases, the electron donor ketyl radicals, formed from the hydrogen abstraction of photoexcited initiator, are oxidized by the iodonium salt. As illustrated on the example of benzophenone in Scheme 3, the resulting carbocations release acids (reaction 11) which may react more favorably with the monomer compared to the sterically hindered carbocations formed from α-cleavage photoinitiators (see reaction 6 in Scheme 2).

Notably, the polydispersities are relatively broader in all indirect systems studied indicating the importance of the reaction steps. Although at longer wavelengths (lower energies), indirect systems involve several reaction sequences i.e. photoinduced radical generation, oxidation and adduct formation. Therefore, growing polymer chains with some differences in chain lengths are formed.

In order to examine the living nature of photoinitiated free radical promoted cationic polymerization of IBVE, time–conversion and conversion–polydispersity index (PDI)–molecular weight (M_n) studies were carried out. Conversion of monomer increased almost linearly with increasing polymerization time (Fig. 2). Conversion–M_n studies indicated

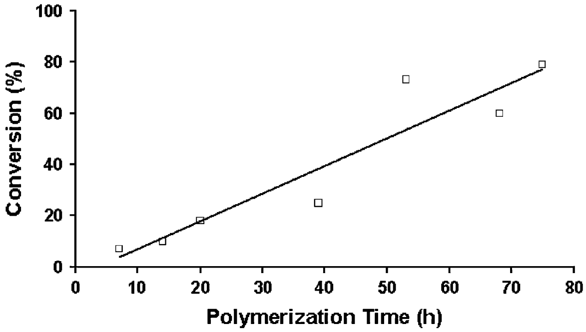
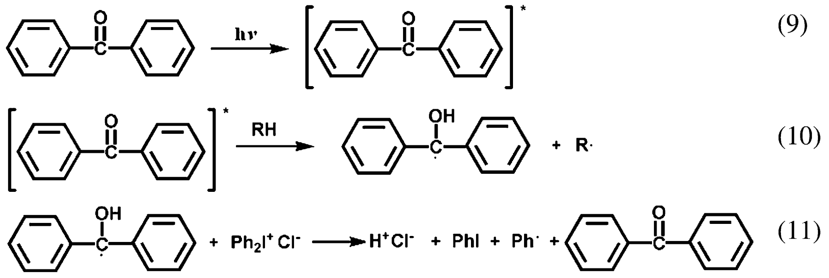


Fig. 2. Time–conversion curve of living cationic polymerization of IBVE carried out in the dark after 1 h photolysis in the presence of DPICl and zinc bromide at −5 °C. Concentrations: $[IBVE] = 3.84$ mol L^{-1}, $[DPICl] = 2.45 \times 10^{-3}$ mol L^{-1}, $[DMPA] = 2.45 \times 10^{-3}$ mol L^{-1}, and $[ZnBr_2] = 3.15 \times 10^{-3}$ mol L^{-1}.



Scheme 3.

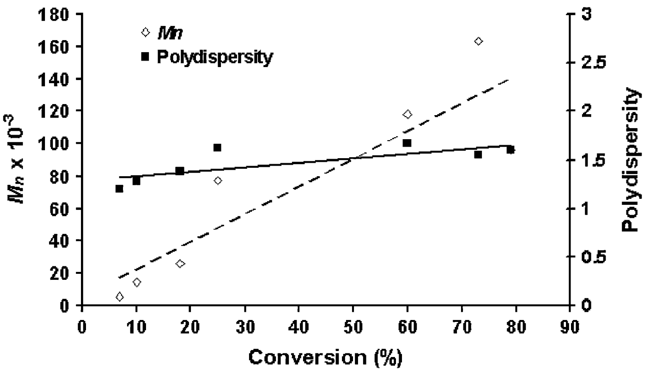


Fig. 3. The dependence of the number-average molecular weight (M_n) and polydispersity index (M_w/M_n) on the percentage of conversion in photoinduced living cationic polymerization of IBVE (see Fig. 2 for the experimental details).

that there was also a linear relationship between conversion and M_n (Fig. 3).

In conclusion, preliminary experimental results fully support the idea that suitable photochemical free radical sources in combination with iodonium salts and zinc halides may be used to promote living cationic polymerization of alkyl vinyl ethers. Mechanistic details remain to be evaluated but for all systems studied, an important feature is the generation of carbocations or acids from free radical sources leading to the formation of monomer adducts which in the presence of zinc salt initiate living polymerization in a manner similar to that described for $HX-ZnX_2$ systems.

Acknowledgements

The authors would like to thank Istanbul Technical University Research Fund for financial support. One of the authors (M.U.K.) thanks Turkish Scientific and Technical Research Council (Tubitak) for financial support by means of a graduate program.

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