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Atom transfer radical polymerization of styrene initiated by triphenylmethyl chloride

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Abstract

Triphenylmethyl chloride (TPMCl) was employed for the first time as the initiator of atom transfer radical polymerization (ATRP) of styrene in the presence of CuCl/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as catalyst and cyclohexanone as solvent. The kinetic plot was first-order with respect to monomer. A linear increase of number average molecular weight (M_n) vs. monomer conversion was observed, and the molecular weight distribution (MWD) was relatively narrow ($M_w/M_n = 1.2$–1.5). ^{1}H NMR spectra revealed the ω-Cl group at the chain end. Another two initiators, benzyl chloride (BzCl) and diphenylmethyl chloride (DPMCl), were also employed in contrast with triphenylmethyl chloride to investigate the influence of phenyl numbers on the polymerization.

Keywords: ATRP; Triphenylmethyl chloride; Diphenylmethylchloride; Benzyl chloride; Styrene

1. Introduction

ATRP is one of the most versatile living/controlled radical polymerization techniques that allow for the preparation of polymeric materials with well-defined molecular weights, compositions, functionalities and architectures [1–5]. The basis of this technique is the reversible transfer of a halogen atom from a monomeric or polymeric alkyl halide (R–X) to a transition metal complex (LM_t^n), generating an organic radical and a transition metal complex ($\mathrm{LM}_t^{n+1}X$) with a higher oxidation state (Fig. 1) [6,7]. To establish the equilibrium between LM_t^n and $\mathrm{LM}_t^{n+1}X$ strongly shifted toward the LM_t^n complex, many factors should be taken into consideration, involving the monomer, initiator with a transferable (pseudo) halogen, catalyst (composed of a transition metal species with any suitable ligand), solvent and temperature [8].

Initiator is of prime importance for successful ATRP. Matyjaszewski and coworkers [9,10] had outlined 10 general guidelines for the selection of the efficient initiators. Generally, alkyl halides RX with either inductive or resonance stabilizing substituents are efficient initiators, such as halogenated alkanes, benzylic halides, α-haloesters, α-haloketones and sulfonyl halides and so on [8]. Benzyl-substituted halides were widely used for styrene, mostly referring to benzyl halides and their derivatives with single phenyl ring connected to the α-carbon,

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$$\mathrm{R\text{-}X} + \mathrm{LM_t^{n}} \rightleftharpoons \mathrm{R^{\bullet}} + \mathrm{LM_t^{n+1}X}$$

Fig. 1. Redox dynamic equilibrium reaction.

including benzyl chloride and bromide, 1-phenylethyl chloride and bromide, etc. Benzhydryl derivatives were also used as the initiators of the polymerization of MMA such as Ph_2CHCl and Ph_2CCl_2 [8,9]. However, triphenylmethylchloride (TPMCl) used as the ATRP initiator has not been reported yet, which may due to the notable stability of triphenylmethyl radical ($Ph_3C^{\bullet}$).

In this paper, TPMCl was employed as initiator for the ATRP of styrene. We found that the polymerization can only proceed using more efficient ligand *N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine (PMDETA) [11] in suitable solvent. Furthermore, the initiators with single phenyl, benzylchloride (BzCl) and double phenyl, benzhydrylchloride (also diphenylchloride, DPMCl) were also investigated in contrast with TPMCl, in order to find the influence of phenyl numbers on ATRP.

2. Experimental

2.1. Materials

Styrene (St) (CP, Shanghai Chemical reagent Co. Ltd., Shanghai, China), PMDETA (98%, Jiangsu Chemical Factory, Liyang, China), cyclohexanone (Shanghai Chemical reagent Co. Ltd., Shanghai, China), were purified by vacuum distillation. CuBr and CuCl (AR, Shanghai Zhenxin Chemical Reagent Factory, Shanghai, China) was stirred in glacial acetic acid, washed with acetone, and then dried under vacuum. TPMCl, DPMCl and BzCl were used as received.

2.2. General procedure

Monomer, solvent, initiator, and catalyst complex was added to a round-bottomed flask. The reaction flask was subjected to several vacuum/nitrogen cycles, and was immersed in an oil bath heated at a certain temperature. Samples for kinetic measurements were taken after a specific time interval from the reaction mixture.

Polystyrene was isolated by precipitation with methanol. The precipitated polymer was solved with THF, precipitated for the second time, and then dried until its weight was constant.

2.3. Characterizations

Monomer conversion was determined by weight method. Molecular weight (M_n, M_w) and molecular weight distribution were measured by GPC with the calibration of the commercially available polystyrene standards and THF as solvent. ^{1}H NMR spectra were taken in an INOVA 400 MHz NMR instrument with deuterated chloroform (CDCl3) as solvent at ambient temperature.

3. Results and discussion

3.1. Effect of catalyst complex

CuX(X = Cl, Br)/bpy was employed as the catalyst system for the ATRP of styrene. It was found that the polymerization can only proceed at a temperature higher than 120 °C. At 120 °C, although the MWD is rather low (<1.3), the conversion and molecular weight change with time irregularly, which indicate that the reaction is not a living/controlled radical polymerization.

Subsequently, PMDETA was selected as the ligand. Fig. 2 shows the relationships between $\ln([M_0]/[M])$ and reaction times catalyzed by CuX (X = Cl,Br)/PMDETA. After an initial induction period, a relatively linear semilogarithmic plot was observed in each case. The induction period at the beginning of the polymerizations may be mainly attributed to the slow initiation of TPMCl. The steric strain effect [9] is adverse for the initiation. Moreover, for the electronic effect, triphenylmethyl radical is very stable and difficult to initiate the polymerization.

The molecular weight increased linearly with conversion with higher values than the theoretical ones (Fig. 3). The initiation efficiency is very low in the initial stage but gradually increasing with conversion. This observation may indicate the occurrence of above-mentioned slow initiation with respect to the fast propagation of

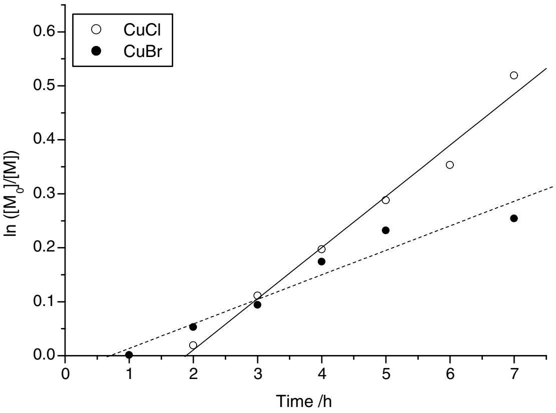

Fig. 2. Kinetics of styrene polymerization initiated by TPMCl with CuX/PMDETA as catalyst. Polymerization conditions: [St]:[CuX]:[PMDETA]:[TPMCl] = 100:1:1:1, 100 °C, cyclohexanone/St(w/w) = 1:1.