

Reverse atom transfer radical polymerization of methyl acrylate using AIBN as the initiator under heterogeneous conditions

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SUMMARY: Reverse atom transfer radical polymerization of methyl acrylate in the presence of a conventional radical initiator (2,2'-azoisobutyronitrile, AIBN) in bulk was successfully implemented via a new polymerization procedure. The system first reacts at 65–70 °C for ten hours, then polymerizes at 100 °C. Various mole ratios of AIBN to Cu^{II}Cl₂ were used in this work, all of which result in a well-controlled radical polymerization with high initiation efficiency and narrow molecular weight distribution, i.e., the polydispersity is as low as $\bar{M}_w/\bar{M}_n = 1.36$.

Introduction

The transition-metal-catalyzed atom transfer radical addition, ATRA, gives a unique and efficient way for carbon-carbon bond formation in organic synthesis¹⁾. Wang and Matyjaszewski^{2,3)} have successfully introduced this method into polymerization chemistry as a novel 'living'/controlled radical polymerization process, i.e., atom transfer radical polymerization, ATRP. Recently, much attention has been paid to the discovery of ATRP. A lot of papers have been published about it during the last two years. It is an important aspect in this research area to find a new initiator system. Wang and Matyjaszewski⁴⁾ reported that in addition to a typical ATRP initiating system (using an alkyl halide, R-X, as an initiator and a transition-metal species complexed with suitable ligand(s), Mtⁿ/Lx, as a catalyst, R-X/Mtⁿ/Lx), a 'living'/controlled polymerization was observed using a conventional radical initiator (AIBN) and a transition-metal compound at higher oxidation state (e.g., Cu^{II}Cl₂) complexed with suitable ligands (e.g., 2,2'-bipyridine, bpy) as a catalyst. This system was used to initiate the polymerization of styrene. However, the authors⁴⁾ failed to control the reaction process when the AIBN/Cu^{II}/bpy-catalyzed ATRP was extended to the polymerization of acrylate monomers. For instance, using AIBN/Cu^{II}Cl₂/bpy (1/10/20) in bulk and at 130 °C, the polymerization of methyl acrylate (MA) was very fast and led to gelation at ca. 40% monomer conversion. Gel permeation chromatography of the tetrahydrofuran-soluble portion gave a much higher molecular weight than calculated according to equation (1). Afterward, Xia and Matyjaszewski⁵⁾ reported that by using alkyl substituted bipyridine ligands, such as 4,4'-nonyl-2,2'-bipyridine (dNbpy), reverse ATRP of methyl acrylate can be carried out under homogeneous conditions. In this work the 'living'/controlled radical polymer-

ization of MA initiated by AIBN/Cu^{II}Cl₂/bpy (1/2/6 mole ratio) in bulk was successfully implemented via a new procedure under heterogeneous conditions, and no gelation was observed.

Experimental part

Materials

Methyl acrylate was vacuum distilled over CaH₂ just before polymerization. AIBN was used after ordinary purification. CuCl₂ and 2,2'-bipyridine were used as received without purification.

Polymerization

Catalyst, ligand, initiator, and monomer were added to a flask with condenser and stirrer. The heterogeneous mixture was first degassed (three times), secondly immersed in an oil bath, heated at 65–70 °C for 10 h, then reacted at 100 °C. After a given time, the flask was opened and tetrahydrofuran (THF) was added to the sample to dissolve the polymer.

Polymer characterization

The monomer conversion was determined by gravimetry. Molecular weight and molecular weight distribution were obtained by gel permeation chromatography (GPC) that was carried out with a Waters 208 instrument, using THF as eluent, and calibration with polystyrene standards.

Results and discussion

Tab. 1 shows the characterization data of poly(methyl acrylate) generated from ATRP catalyzed by AIBN/Cu^{II}Cl₂/bpy in bulk. The mole ratio of Cu^{II}Cl₂ versus AIBN is not a critical parameter for the 'living'/controlled poly-

Tab. 1. Characterization data of poly(methyl acrylate) bulk polymerization initiated with AIBN/CuCl₂/bpy

[AIBN]	[CuCl ₂]	[bpy]	Time in h	Conv. in %	$\bar{M}_{n,th}^a)$	$\bar{M}_{n,GPC}$	\bar{M}_w/\bar{M}_n
	mol/L						
0.0155	0.031	0.093	12	93	28638	29900	1.46
0.0155	0.062	0.186	18	89	27406	28600	1.42
0.0155	0.093	0.279	31	92	28330	29000	1.36
0.0155	0.124	0.372	41	91	28022	28700	1.39

^{a)} Cf. Eq. (1).

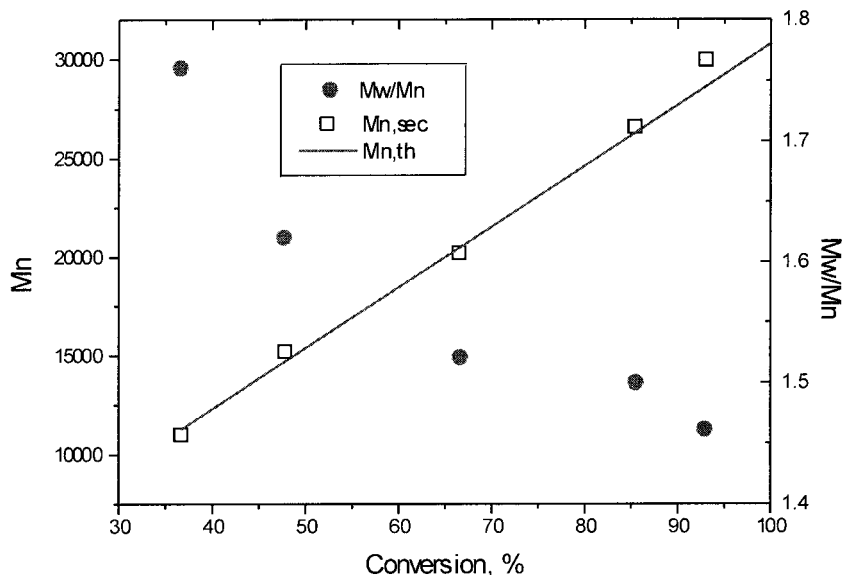


Fig. 1. Evolution of molecular weight, \bar{M}_n , and molecular weight distribution, with monomer conversion for the bulk polymerization of MMA initiated with AIBN/CuCl₂/bpy. [MA] = 11.1 mol/L, [AIBN] = 0.0155 mol/L, [CuCl₂] = 0.031 mol/L, [bpy] = 0.093 mol/L

merization by using the new polymerization procedure. The increase in [Cu^{II}Cl₂]/[AIBN] ratio did not facilitate the control of the polymerization. All mole ratios of Cu^{II}Cl₂ to AIBN used in this work result in a well-controlled radical polymerization with high initiation efficiency and a polydispersity as low as $\bar{M}_w/\bar{M}_n = 1.36$.

Fig. 1 shows that the measured molecular weight linearly increases with the monomer conversion, and matches the theoretical value calculated from Eq. (1) for bulk polymerization of MA initiated with AIBN and in the presence of 2 molar equiv. of Cu^{II}Cl₂ and 6 molar equiv. of bpy at 100 °C.

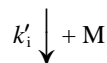
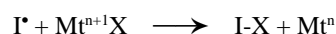
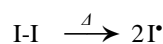
$$\bar{M}_{n,th} = 86 \times \{[M_0]/(2[AIBN])\} \times \text{conversion} \quad (1)$$

where 86 is the molecular weight of MA and [M₀] is the initial concentration of monomer.

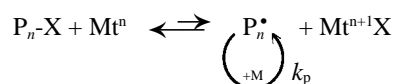
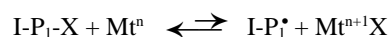
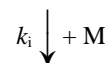
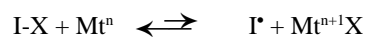
These experimental data indicate that the polymerization proceeds via a 'living'/controlled polymerization mechanism in the bulk polymerization of MA initiated with the AIBN/Cu^{II}Cl₂/bpy system. Furthermore, a very good correlation between the theoretical molecular weight and the experimental one was found up to 3×10^4

with $\bar{M}_w/\bar{M}_n \leq 1.46$ (Tab. 1), indicating a high initiation efficiency of AIBN. The reaction scheme is suggested as below:

Initiation and termination at lower temperature:



Initiation and propagation at higher temperature:



where P_n is a polymer molecule with degree of polymerization n .

The present outcomes can be explained in terms of this scheme. It is known that $\text{Cu}^{\text{II}}\text{Cl}_2$ is a strong and efficient inhibitor for radical polymerization under usual conditions⁶. When the polymerization of MA proceeds at 65–70 °C, it enables slower decomposition of AIBN which allows to dissolve $\text{Cu}^{\text{II}}\text{Cl}_2/\text{bpy}$ at a rate comparable to AIBN consumption. So the highly oxidized transition-metal $\text{Cu}^{\text{II}}\text{Cl}_2$ is a strong and efficient inhibitor to the polymerization of MA initiated by AIBN, which donates the halogen atom Cl to the initiating or propagating radicals, I^\bullet or I-P^\bullet , forming the reduced transition-metal species, Cu^{I} , and the dormant species, I-Cl and P-Cl. At lower temperature, 65–70 °C, the covalent species I-Cl and P-Cl are rather stable, therefore the reduced transition-metal species, Cu^{I} , can not promote the ATRP process as in the ‘living’/controlled radical polymerization initiated by R-X/Mt/Lx at higher temperature. After ten hours at 65–70 °C, most of AIBN is exhausted while the reduced transition-metal species, Cu^{I} , and the dormant species, I-Cl and P-Cl, are accumulated. During this period the inhibited reaction is predominant, little polymer is

generated. The fast ATRP needs a higher temperature. When the system is heated to 100 °C, however, in the presence of a coordinative ligand a reversible activation of the resulting alkyl chlorides occurs, and the polymerization of the system proceeds via the reverse ATRP mechanism.

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