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Controlled radical polymerization of methacrylates at ambient temperature and the synthesis of block copolymers containing methacrylates

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Abstract

The controlled radical polymerization of methyl methacrylate (MMA) and 2-hydroxy ethyl methacrylate (HEMA) were successfully performed at ambient temperature. MMA was polymerized in acetonitrile with ethyl-2-bromopropionate (EPN-Br)/CuCl/2, 2′-bipyridyl (bpy) at 40°C. The final polymer was with a narrow molecular weight distribution ($M_w/M_n < 1.5$) and controllable molecular weight. The controllable nature might have been contributed mainly by the high value of dielectric constant of acetonitrile. The bulk polymerization of HEMA, a monomer with a high value of dielectronic constant, can be well controlled with EPN-Br/CuCl/ bpy at 20°C. The halogen terminated PMMA and PSt were then used as macroinitiators to copolymerize with some other monomers. As a result, some block copolymers, such as PMMA-b-PSt, PMMA-b-PHEMA and PSt-b-PHEMA, were synthesized.

Keywords: Controlled radical polymerization; Block copolymers; Copper halides

1. Introduction

Copper halides (CuX) and 2, 2′-bipyridyl (bpy) can be employed to control the polymerization of a wide range of vinyl monomers efficiently in conjunction with alkyl halides(R–X) as initiators, and is known as atom transfer radical polymerization (ATRP). The radical centers (R·) in ATRP was considered to be created by the reaction of alkyl halide (R–X) with CuX/bpy (Scheme 1) [1].

As shown in Scheme 1, the radical concentration is controlled by a fast reversible equilibrium between the dormant species (DS) and the active species (AS). Therefore, termination reactions are suppressed, resulting in a ''living'' polymerization in nature.

Matyjaszewski reported that PMMA was able to be synthesized with a narrow molecular weight distribution (MWD) by using a homogeneous ATRP catalytic system based on copper bromide and a substituted bipyridyl [2]. Subsequently, Haddleton employed 2-pyridinecarbaldehyde imine in place of bipyridines in conjunction with copper bromide and bromides leading to a well control of the polymerization of MMA [3]. However, the reactions have to be carried out at an elevated temperature (90°C). The polymerization of MMA catalyzed by CuX/bpy have not been performed at an ambient temperature, although it has been successfully carried out in the system catalyzed by Ni and Pd. [4,5]. In a previous article, [6,7] we also reported that the ''living'' polymerization of MMA in acetontrile, a solvent with a high dielectronic constant, proceeded successfully in the system of ethyl-2-bromopropionate (EPN-Br)/CuCl/bpy at 80°C within a few hours. UV study shows that acetonitrile is advantageous for the catalyst (CuCl/bpy) to form the catalyst active structure, $[Cu(I)bpy_2]X^-$, at reduced temperature [6,7]. This implied that the ATRP of MMA might be performed at even lower temperatures. In contrast, the ATRP of 2-hydroxyethyl methacrylate (HEMA), a monomer with a high value of dielectric constant, has not been reported up to date, although ATRP of hydroxethyl acrylate (HEA) initiated by methyl 2-bromopropionate (MBP)/CuBr/4,4′-(5-nonyl)-2,2′-bipyridine (dNbipy) has been successfully performed at 90°C [8].

In the present work, the polymerization of MMA in acetontrile and the bulk polymerization of HEMA in EPN-Br/CuCl/bpy was attempted at an ambient temperature, because the high dielectronic constant of solvent (acetonitrile) or monomer (HEMA) would make it easy to form a catalyst active structure [6,7].

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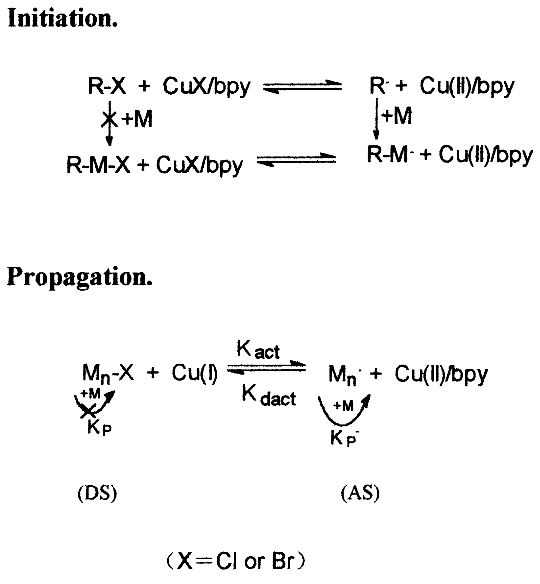


Scheme 1.

One of the most important purposes of the ''living'' polymerization is to synthesize well-controlled polymers, especially, the block copolymers with different monomer units in the blocks. Although various block copolymers have been synthesized by a combination of different polymerization techniques [9–11], it is not easy to synthesize block copolymers with well-defined structures, especially, PSt-b-PMMA and PSt-b-PHEMA.

PMMA-b-PHEMA and PSt-b-PMMA can be synthesized under rigorous conditions through GTP and anionic polymerization, respectively. Recently, radical living polymerization with a Ru-complex was reported to synthesize PSt-b-PMMA [12]. Silylated HEMA was used in the synthesis of PSt-b-PHEMA by an anionic method in which species transformation and hydrolysis had to be employed [13]. Taking the long pot-life of species in ATRP into consideration, we shall develop a method to utilize HEMA directly for preparing block copolymers containing HEMA.

For the objective of preparing the block copolymers, PSt-Br and PMMA-Cl was used as the macroinitiators to polymerize MMA, St, HEMA, respectively. As a result, block copolymers with well-controlled structures, such as PSt-b-PMMA, PMMA-b-PHEMA and PSt-b-PHEMA, could be synthesized under mild conditions.

2. Experimental section

2.1. Materials

EPN-Br was commercially available, and used without additional treatment. Copper chloride (CuCl), copper bromide (CuBr) was purified according to the literature [14]. 2,2′-Bipydyl (bpy) was commercially available, and recrystallized several times from acetone and dried in vacuum before use. Methyl methacrylate (MMA) was vacuum distilled over CaH_2 under argon before polymerization. HEMA was purified as follows: after dissolution of the monomer in water (1/4), hydroquinone (0.1%) was added to prevent polymerization; the solution was extracted with hexane (10 times) to remove diacrylate and ethylene glycol; the aqueous solution was salted (250 g/l) and the monomer removed by ether extraction (four times); after the addition of hydroquinone and drying on $CaSO_4$, the ether solution was evaporated and the monomer kept over molecular sieves; the monomer was distilled just before use under vacuum. Acetonitrile and acetone were distilled over CaH_2.

2.2. Homopolymerization

The general procedure was as follows: CuX, and bpy were added in a baked glass tube and sealed with a rubber septum. The glass tube was then degassed under vacuum and filled with argon, this was done three times. The degassed MMA or HEMA, initiator, solvent was then added by a syringe technique, and then immersed in an oil bath and heated at the desired temperature. After a certain

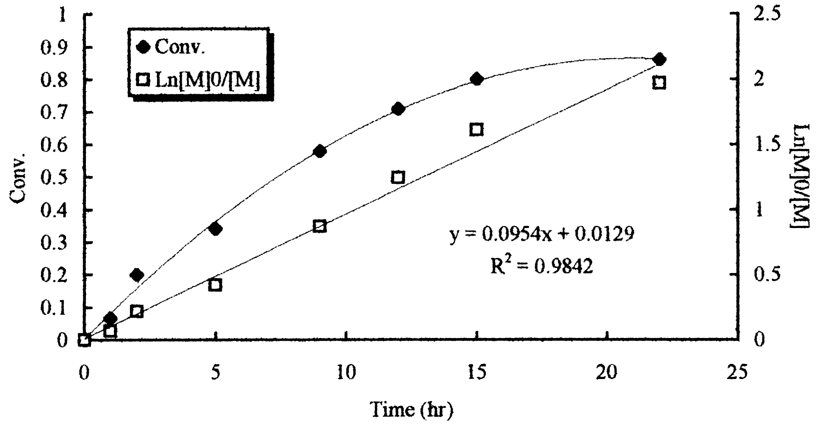


Fig. 1. The polymerization kinetics of MMA initiated by EPN-Br/CuCl/bpy in acetonitrile at 40°C. $[MMA]_0 = 4.65$ M, $[EPN\text{-}Br]_0 = [CuCl]_0 = 0.038$ M, $[bpy]_0 = 0.116$ M.

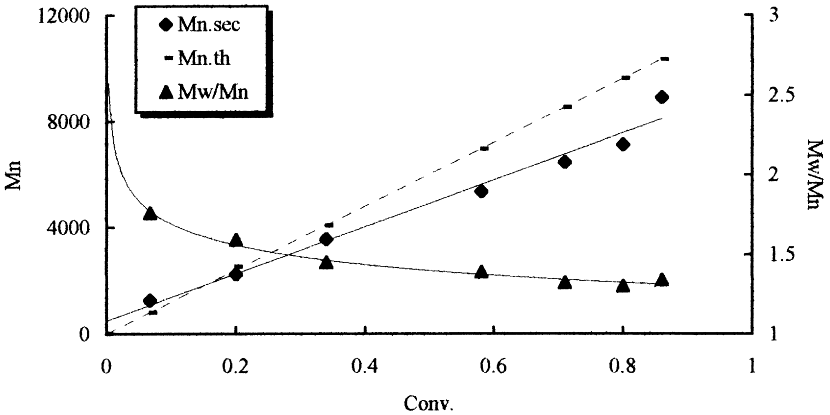


Fig. 2. $M_{n.}$ and M_w/M_n dependence on monomer conversion for the polymerization of MMA initiated by EPN-Br/CuCl/bpy in acetonitrile at 40°C. $[MMA]_0 = 4.65$ M, $[EPN\text{-}Br]_0 = [CuCl]_0 = 0.038$ M, $[bpy]_0 = 0.116$ M.

time, the tube was opened and THF was added to the sample to dissolve the polymer.

2.3. Block copolymerization

The procedure of the block copolymerization was similar to that of the homopolymerization as described earlier except the macroinitiator, PMMA-Cl or PSt-Br, was added together with the catalyst (CuX/bpy) at first.

2.4. Characterization

The conversion was determined gravimetrically and/or Gas Chromatography. Molecular weight and MWD were measured using Waters 150C-ALC /GPC with Waters Styragel® HT2, Styragel® HT4 columns. The molecular weight was calibrated by polystyrene standards with or without rectification. The content of halogen end group was analyzed according to our previous article [7,15].

3. Results and discussion

3.1. Homopolymerization

Acetontrile was once used as an additive in the ATRP of St, the result shows that it has almost no influence on the polymerization [16]. However, when acetonitrile was used as a solvent in the polymerization of MMA, the polymerization was easily controlled. The benefit of acetonitrile might be caused by its high dielectric constant and some other uncertain factors, which make it easy for CuCl/bpy to form $[Cu(I)bpy_2]$ [6,7]. When we tried to polymerize MMA in acetontrile at 40°C in the presence of EPN-Br/CuCl/bpy, a controlled polymerization was achieved. As shown in Fig. 1, a linear relationship of $\ln[M]_0/[M]$ vs. reaction time indicates that the kinetics is first order with respect to monomer concentration. The molecular weight of the PMMA increases with the monomer conversion and matches the theoretical one (calculated base on the molar concentration of initiator), meanwhile, the MWD remains narrow during the polymerization process (Fig. 2).

Table 1
The results of polymerization of HEMA initiated by EPN-Br: CuCl: bpy (1 : 1 : 3) at 20°C

Reaction time/min	Conv. (%)	Extension time[a]/min	$M_{n.}$[b]	M_w/M_n
20	5.9	19.92	1559	1.83
90	17.5	18.35	3014	1.69
150	44.2	17.35	6982	1.37

[a] The peak of GPC trace.

[b] Calibrated by polystyrene standards without rectification.

When the bulk polymerization of HEMA, a monomer with a high value of dielectric constant, was performed at 40°C in the same initiation system all monomers were consumed within 15 min, and a crosslinked polymer was produced. By reducing the reaction temperature to 20°C, we carried out the bulk polymerization of HEMA smoothly within 2 h. As shown in Table 1, the molecular weight of the polymer (PHEMA) increases with the reaction time extended, and the MWD of the polymer narrowed from 1.83 to 1.37 with a rise in monomer conversion. On further extending the polymerization time, an insoluble product was produced, which might be caused by some side reaction.

The results suggest that the controlled polymerization of MMA and HEMA catalyzed by CuX/L are obtained at an ambient temperature and the high value of dielectric constant of the solvent or the monomer could play an important role by way of affecting the formation of a catalyst active structure.

According to the theoretical analysis of radical living polymerization, it is important for ATRP to get a higher value of K_p/K_t at higher reaction temperatures, provided the active species in ATRP is a free radical [17,18]. However, the controlled polymerization of MMA [19,4,5] and HEMA have been performed at ambient temperatures by our group and other groups, especially the final products were obtained with a narrow MWD. The results implied that the active species in these

Table 2
The results of the synthesis of the block copolymers using P–X as macroinitiator, CuCl/bpy as a catalyst[a]

Macroinitiators			2nd monomers	T (°C)	t (h)	Block copolymers	
P–X	M_n[b]	M_w/M_n				M_n[b]	M_w/M_n
PSt-Br	6401	1.31	MMA	40	21	13,467	1.33
PSt-Br	6401	1.31	HEMA	40	48	74,08	1.28
PMMA-Cl	6347	1.27	HEMA	25	8	13,165	1.47
PMMA-Cl	6347	1.27	HEMA	25	24	26,362	1.54

[a] P–X : CuX : bpy = 1 : 1 : 3.
[b] Calibrated by polystyrene standards without rectification.

systems might have some undiscovered special features different to the free radical species.

3.2. The synthesis of block copolymers

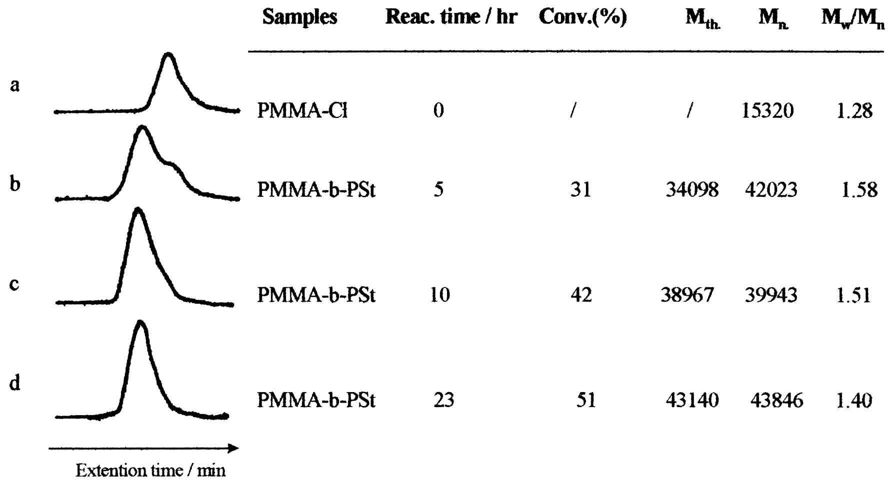
In order to synthesize block copolymers, a macroinitiator technique was used in our experiments. The macroinitiator was the halogen-terminated polymer (P–X) which is the product of the homopolymerization of MMA or St in R–X/CuX/bpy system. PMMA-Cl was prepared through the polymerization of MMA in the presence of EPN-Br/CuCl/bpy. The Cl end-group, instead of Br end-group, was proved by halogen analysis [6,7]. PSt-Br was synthesized through the polymerization of St in EPN-Br/CuBr/bpy at 110°C. The content of the halogen end group was measured by using the oxygen–bomb method. The molecular weights based on the halogen content were identical to the GPC results. The values of M_n and M_w/M_n of the two kinds of macroinitiators (PMMA-Cl, PSt-Br) are listed in Table 2.

In order to synthesize PMMA-b-PSt, the polymerization of St was performed at 110°C, in which PMMA-Cl was used as the macroinitiator and CuBr/ bpy was used as the catalyst.

Fig. 3 shows the GPC traces and the relationship between the molecular weight control and the reaction time. As shown in Fig. 3, the molecular weights of the block copolymers are higher than that of the macroinitiators and rise with the reaction time extended, suggesting that the block copolymer is actually synthesized by PMMA-Cl as a macroinitiator. There is a shoulder peak in the GPC trace (Fig. 3(b)), which indicates the PMMA-Cl was not consumed completely. Therefore, the molecular weight of the copolymer is higher than that of theoretical one (calculated base on the molar concentration of PMMA-Cl) and the MWD is broader. With the prolonging the reaction time, the GPC traces are converted into a monopeak (Fig. 3(c) and (d)), suggesting that the initiation was almost completed. Therefore, the molecular weight of the copolymers matches the theoretical one and the MWD drops to 1.40 after the polymerization proceeding for 23 h.

The results show PMMA-b-PSt with a well-controlled structure can be synthesized with the procedure: firstly, carrying out the polymerization of MMA in acetonitrile at 40°C, and then polymerizing St by using the resulted PMMA-Cl as macroinitiator at 110°C.

Indeed, the PMMA-b-PSt can also be synthesized from the PSt-Br macroinitiator. Table 2 shows that PMMA-b-PSt was prepared with a narrow MWD ($M_w/M_n = 1.33$) through the polymerization of MMA initiated by PSt-Br/CuCl/bpy



	Samples	Reac. time / hr	Conv.(%)	$M_{th.}$	M_n	M_w/M_n
a	PMMA-Cl	0	/	/	15320	1.28
b	PMMA-b-PSt	5	31	34098	42023	1.58
c	PMMA-b-PSt	10	42	38967	39943	1.51
d	PMMA-b-PSt	23	51	43140	43846	1.40

Fig. 3. The relationship between the GPC traces and the reaction time in the ATRP of styrene initiated by macroinitiator (PMMA-Cl) and catalyzed by CuBr / bpy at 110°C.

at 40°C (Table 2). Based on a similar technique, the synthesis of PSt-b-PHEMA and PMMA-b-PHEMA was fulfilled (Table 2).

Table 2 shows, the molecular weights of the block copolymers are higher than those of the macroinitiators (P–X) and the MWD is narrow. All GPC results for the copolymers in Table 2 show that the monopeaks and the extension time is smaller than that of the macroinitiators. This indicates that P–X can efficiently initiate the vinyl monomers to synthesize some kinds of block copolymers.

4. Conclusion

The controlled polymerization of MMA in acetontrile and the controlled bulk polymerization of HEMA were successfully performed at 40°C and 20°C, respectively. In the polymerization, the high value of the dielectric constant of the solvent or monomer might be an important factor. Moreover, the PMMA-b-PSt, PMMA-b-PHEMA, PSt-b-PHEMA are synthesized with a narrow MWD.

Acknowledgements

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