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Reverse Atom Transfer Radical Polymerization of MMA Initiated by Triphenylmethane

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Summary

Triphenylmethane (TPM) was successfully employed for the reverse atom transfer radical polymerization (RATRP) of methyl methacrylate (MMA) in the presence of $CuCl_2$/ pentamethyldiethylenetriamine (PMDETA). The conventional free radical polymerization (CFRP) of MMA was firstly carried out in the presence of TPM, proving that TPM can initiate the polymerization. The RARTP of MMA in cyclohexanone (CHO) exhibited the living/controlled characteristics: the first-order kinetics with respect to monomer, linear increase of number-average molecular weight (M_n) with conversion, narrow polydispersity index (PDI) (<1.4) and successful chain extension. The possible mechanism was also proposed.

Introduction

As one of the most successful "living"/ controlled polymerizations, atom transfer radical polymerization (ATRP) has drawn more and more attentions since its first applications in 1995 [1-3]. ATRP enables formation of well-defined polymers with controlled topology, composition, and functionality [4,5]. A conventional ATRP system is composed of the monomer, an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand). However, it has two major problems: the toxicity of the halide species RX and the oxidation of the catalyst Mt^n/LX by the oxygen in air [6].

To overcome the disadvantages of conventional ATRP, Matyjaszewski [7-8] and Teyssie [10] developed reverse ATRP (RATRP). RATRP differs from normal ATRP in its initiation process, where a conventional radical initiator and a metal salt at higher oxidation state are used. The most popular initiators of RATRP involves azo- and peroxide compounds, such as BPO and AIBN [8,9]. Many iniferters, mostly the hexasubstituted ethanes, having an irreversible decomposition step were also reported, such as TD [11], DCDPS [12], DMPA [13], DCDTS [14].

Known as an "amphihydric" compound, triphenylmethane (TPM) can undergo either heterolytic cleavage to give a triarylcation and the corresponding anion or homolytic cleavage to give radicals [15-17]: a stable trityl radical (Tr·) and an active radical H·[26]. The bond dissociation energy (BDE) value of TPM is as low as 81kcal/mol [18]. In our previous work [19], we have used triphenylmethyl chloride as the initiator of normal

ATRP, which showed that Tr· is able to initiate the polymerization. Herein, we firstly utilized TPM as the initiator for conventional free radical polymerization (CFRP) of MMA. Subsequently, the RATRP of MMA was conducted in cyclohexanone (CHO) using TPM as the initiator. As a result, the RATRP exhibited the typical characteristics of living/controlled polymerization. Although low initiation efficiency was observed, this new type, commercially cheap and available compound provided an alternative of RATRP initiator.

Experimental

Materials

Methyl methacrylate (MMA) (CP,Shanghai Chemical reagent Co. Ltd., Shanghai, China), N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) (98%, Jiangsu Chemical Factory, Liyang, China), CHO (Shanghai Chemical reagent Co. Ltd., Shanghai, China), were purified by vacuum distillation. $CuCl_2·2H_2O$ and Triphenylmethane (TPM) (C.P, Shanghai Zhenxin Chemical Reagent Factory, Shanghai, China) were used as received.

General polymerization procedure

A typical polymerization procedure is described as follows:
100mmol MMA, 10g CHO, 1mmol $CuCl_2·2H_2O$, 1mmol TPM and 1mmol PMDETA 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 80°C. Samples for kinetic measurements were taken after a specific time interval from the reaction mixture.
PMMA 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.

Characterizations

Monomer conversion was determined by weight method. Molecular weight (M_n, M_w) and PDI were measured by gel permeation chromatography (GPC) with the calibration of the commercially available poly(methyl methacrylate) standards and THF as solvent. ^{1}HNMR spectra were taken in an INOVA 400 MHz NMR instrument with deuterated chloroform ($CDCl_3$) as solvent at ambient temperature.

Results and Discussion

Conventional Free Radical polymerization

As we mentioned above, the dissociation of TPM results in two radicals. To investigate whether these radicals can be utilized as the initiator, we firstly conducted the CFRP of MMA in CHO. Tab 1 summarizes the results at 70°C and 90°C, respectively.

Tab 1. Conventional free radical polymerization of MMA initiated by TPM

Temperature, °C	$[TPM]_0$, mmol	Time, h	Conversion, %	M_n	PDI
70	0	30	0	-	-
70	1	27.6	14.6	99700	2.7
70	1	29	16.3	102300	2.7
70	1	34.2	18.4	88600	2.9
90	1	2	6.19	87900	2.7
90	1	3.65	13.6	83100	2.6

Reaction conditions: $[MMA]_0$=100mmol, W_{CHO}=2g.

In Tab 1, MMA failed to polymerize at 70°C in the absence of TPM. By contrast, although the rate was very slow, the polymerization was induced by the addition of TPM at the same temperature. When increasing the temperature to 90°C, the rate was greatly enhanced, which may due to the accelerated dissociation of TPM. The M_n remained constant and the PDI were rather broad (M_w/M_n>2.6) in both cases, which is corresponding to the characteristics of CFRP.

Therefore, it is concluded that TPM may be used as the initiator of CFRP of MMA. Our following work was then focused on the RATRP using this compound as the initiator.

RATRP of MMA initiated by TPM

Effect of solvent

The RATRP of MMA in the presence of TPM/$CuCl_2$/PMDETA was firstly carried out in various solvent, including bulk, anisole, toluene, DMF, acetonitrile, 1,4-dioxane, acetophenone, acetone, and CHO etc. The reactions were all performed at 80°C. After stirred and heated for several minutes, the reaction mixtures in DMF, acetonitrile, acetophenone and CHO turned to be homogeneous, while in other solvents the mixtures remained heterogeneous. After 7h, the reactants were all poured into methanol to precipitate the polymers. However, only in CHO the PMMA can be obtained (conversion=90.5%, M_n=35300, PDI=1.4). This indicates that the polymerization may only occurred in CHO and is strongly solvent-dependent.

It has been suggested that suitable solvent may increase the solubility of the catalyst and also modify the concentrations of Cu(I) and Cu(II) in the polymerization system, in this way, the polymerization rate can be increased and the PDI can be reduced [20-23]. In this work, however, it is obvious that the solubility of catalyst should not be crucial, since the polymerization failed in DMF with higher polarity. Matyjaszewski K [24] et al reviewed the structure features of copper complexes with different ligand in ATRP. The structure of copper complex may be different in different solvent. The solvent is very likely to affect the redox properties of the copper complex and therefore its catalytic activity. In our work, it is very possible that the participation of CHO may activate the initiation and subsequently induce the polymerization.

Effect of temperature

The RATRP of MMA in the presence of TPM/$CuCl_2$/PMDETA was performed at 70, 80 and 90°C respectively, and the results are summarized in Fig 1 and Fig 2. It should be mentioned that, the precipitation of the polymer in methanol can lead to underestimated conversion, overestimated experimental molecular weights and artificially narrowed polydispersity. Nevertheless, since all the treatments were conducted under the similar conditions, the trend of the variation of conversion and M_n should not be affected.

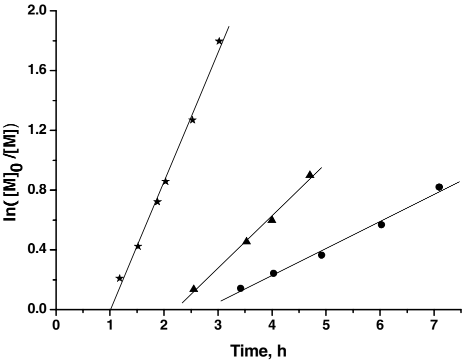


Fig 1. Kinetic plot for RATRP of MMA initiated with TPM/$CuCl_2$/PMDETA at different temperature: 70°C (●), 80°C (▲) and 90°C (★). Other conditions: W_{MMA}:W_{CHO}=1:1, $[MMA]_0$:$[TPM]_0$:$[CuCl_2]_0$:$[PMDETA]_0$=250:1:1:1.

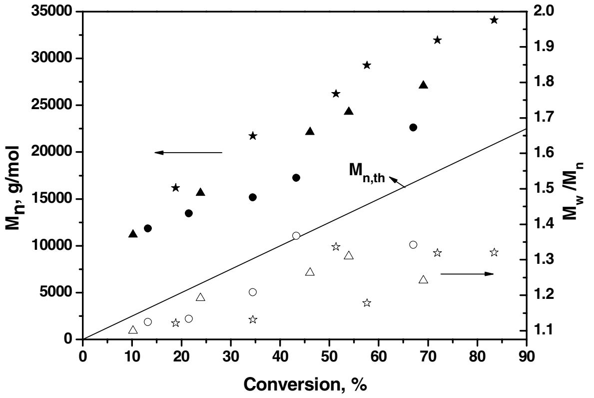


Fig 2. Dependences of M_n and M_w/M_n on conversion for RATRP of MMA initiated with TPM/$CuCl_2$/PMDETA at different temperature: 70°C (●, ○), 80°C (▲, △) and 90°C (★, ☆). Other conditions were given in caption for Fig 2. The straight line is the theoretical plot, where $M_{n,th}$=$[MMA]_0$/(2$[TPM]_0$)*Conversion*MW(MMA).

Fig 1 demonstrates the kinetic plots at different temperatures. The linear semilogarithmic plots of ln($[M]_0$/[M]) vs time indicate constant concentration of growing species in all cases. The rate of polymerization was accelerated with increasing temperature. Additionally, induction periods were observed but were shortened by the elevated temperature. Two reasons should be responsible for the induction period. Firstly, the dissociation of TPM was slow. Secondly, in the initial stage, $CuCl_2$ was in great excess compared to the radicals generated. As a result, the polymerization was retarded/inhibited during this induction period[8]. The increase of temperature can accelerate the generation of radical, and thus the induction period was shortened.

Fig 2 displays the number-average molecular weights and PDI vs conversion. In each case, the M_n increases linearly with conversion, which indicates a constant number of chains, and the PDI is rather narrow (<1.4). However, the M_n measured by GPC is much higher than the theoretical value. This may be caused by some side reactions, mostly due to the high activity of H· radical. TPM is thermally dissociated to generate Tr· and H·. Once generated, the latter is expected to add to the double bond of monomer to initiate the polymerization. However, most of them will be consumed by other side reactions, which should be the main reason of low initiation efficiency. As for Tr·, it is notably inactive, and relatively difficult to initiate the polymerization, which also cause the low initiation efficiency [19]. Moreover, at the same conversion, the M_n value increases with increasing temperature. That is, the higher the temperature, the lower the initiation efficiency. At higher temperature, dissociation of TPM is accelerated, resulting in a relatively high concentration of H·, and therefore the occurrence of radical coupling arises, resulting in a lower initiation efficiency.

Effect of monomer-to-initiator molar ratio

To investigate the effect of monomer-to-initiator molar ratio, three different concentrations of catalyst were performed in RATRP of MMA, when keeping other factors unchanged. The kinetic plot is present in Fig 3, and the dependences of M_n and M_w/M_n on monomer conversion are shown in Fig 4, respectively.

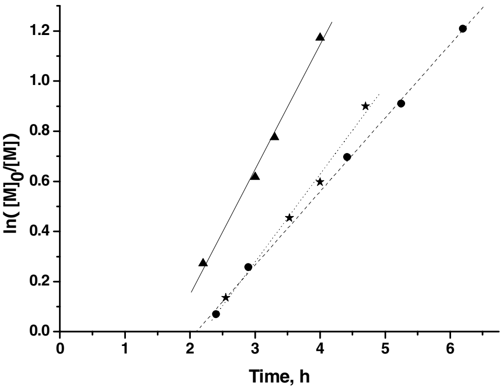


Fig 3. Kinetic plot for reverse ATRP of MMA initiated with TPM/$CuCl_2$/PMDETA in different monomer-to-initiator molar ratio. $[MMA]_0$:$[TPM]_0$=50:1(●), 100:1(▲) and 250:1(★). Other conditions: at 80°C, $[TPM]_0$:$[CuCl_2]_0$:$[PMDETA]_0$=1:1:1, W_{MMA}:W_{CHO}=1:1.

Fig 3 illustrates the kinetic plots. In each case, the linear semilogarithmic plot of ln([M]o/[M]) vs time indicates constant concentration of growing specie. The rate of polymerization varies at different ratio, among which that at 100:1 is the fastest and the corresponding induction period is also the shortest. This is explained by the concentration of initiator or $CuCl_2$. When the monomer-to-initiator molar ratio changed from 250:1 to 100:1, the concentration of initiator also increased, thus the rate of polymerization increased, followed by the shortened induction period. However, when the ratio was 50:1, corresponding to the excessively high concentration of inhibitor $CuCl_2$, the rate of Polymerization is slowed down and exhibits long induction period.

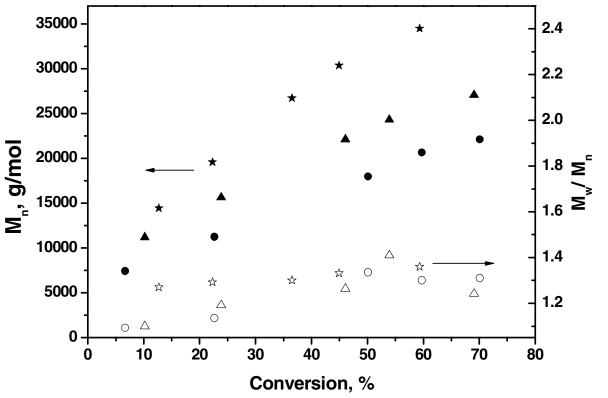


Fig 4. Dependences of M_n and M_w/M_n on conversion for reverse ATRP of MMA initiated with TPM/CuCl$_2$/PMDETA in different monomer-to-initiator molar ratio. [MMA]$_0$:[TPM]$_0$=50:1 (●, ○), 100:1(▲, △) and 250:1(★,☆). Other conditions were given in caption for Fig 4.

From Fig 4, it can be concluded that each of the polymerizations proceed in a controlled manner: linear increase of M_n with conversion and low PDI (M_w/M_n<1.4). With the increase of monomer concentration, the M_n value also increases at the same conversion. When the ratios are 50:1 and 100:1, the PDI are narrower, indicating that the polymerizations were better-controlled.

Characterization of Polymer

The polymer prepared by reverse ATRP of MMA initiated with TPM/CuCl$_2$/PMDETA was characterized by ^{1}HNMR as shown in Fig 5.

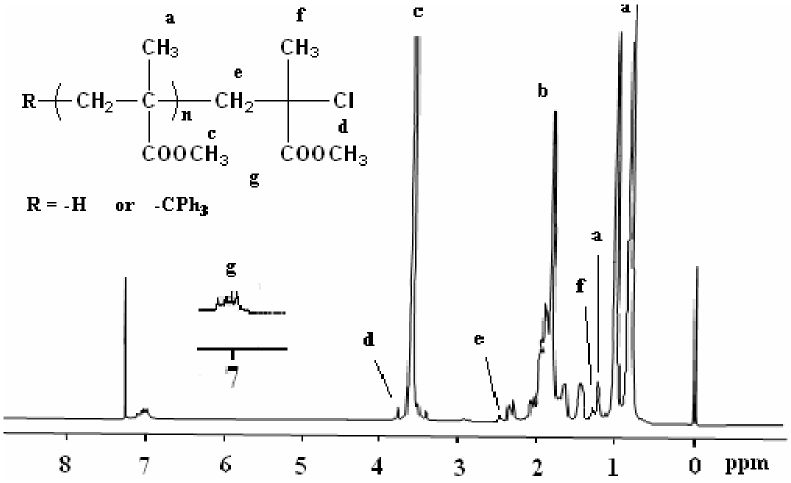


Fig 5. 400MHz ^{1}H NMR spectrum (in CDCl$_3$) of PMMA ($M_{n,GPC}$=9600, M_w/M_n=1.3).

In Fig 5, the signals at 0.84-1.21, 1.43-2.07, and 3.41-3.60 ppm are assigned to the protons of methyl groups of -C(CH_3)(COOCH$_3$), methylene groups of -CH_2-, and methoxy groups of -C(CH$_3$)(COOCH_3), respectively. In particular, the signal at 3.78

ppm (H_d) is for the protons of the methoxy group, that at 2.50 ppm (H_e)is for the methylene protons, and that at 1.26 ppm (H_f) exhibits the characteristic chemical shifts of the terminal MMA unit capped with an ω-end chlorine. More importantly, the signals at about 7ppm (H_g) are attributed to the protons of the phenyl rings. Thus, triphenylmethyl group is at the α-end while chlorine atom is at the ω-end of PMMA. The calculated M_n by NMR is $M_{n,NMR}$= 13000. Obviously, this value is much higher than that by GPC ($M_{n,GPC}$=9600). The deviation can be explained by the partial existen ce of alpha-hydrogen-ended polymer. Moreover, the ratio of proton number at 7ppm and 1.26ppm is H_g:H_f=3.9:1, Assuming all the polymer chain ends were triphenylmethyl-capped and no Cl end groups were lost, the H_g:H_f ratio should be 5:1, and therefore the percentage of triphenylmethyl-ended polymer is 78%.

Chain Extension

To further confirm the living characteristic of the polymerization, we conducted a reaction of chain extension, using the polymer as macroinitiator to initiate the conventional ATRP of St in the presence of CuCl and 2,2'-bipyridine (bpy). Fig 6 shows the GPC curves of the macroinitiator and the final block copolymer Poly(MMA-b-St) obtained after 26.5% conversion of St. M_w/M_n of the final polymer (1.3) was a little broader than that of the macroinitiator (1.2), but the M_n value increased to 24,300 from 16,200. The success of the chain extension further proved the characteristics of living polymerization in this system of the reverse ATRP of MMA initiated with TPM/$CuCl_2$/PMDETA.

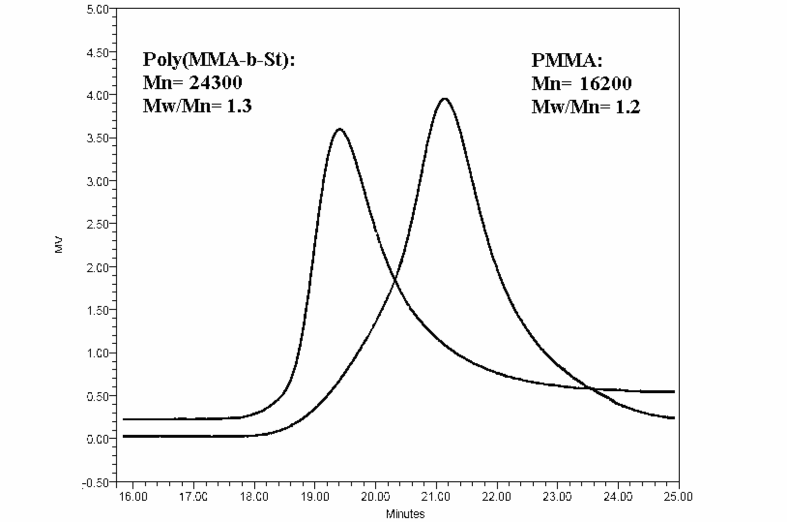
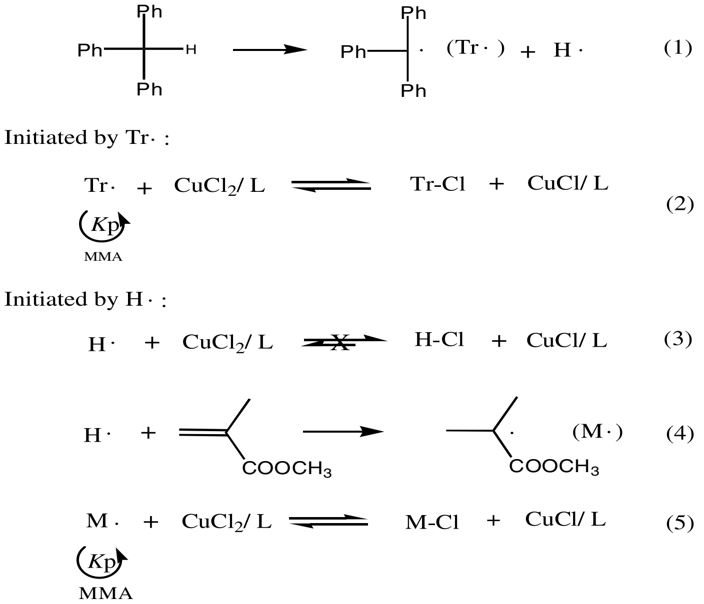


Fig 6. GPC curves of the PMMA as macroinitiator and the block copolymer after precipitation in methanol. Reaction conditions: $[St]_0$:$[macroinitiator]_0$:$[CuCl]_0$:$[bpy]_0$=300:1:1:3, CHO:St(w/w)=1:1, at 110°C for 3 hours.

Plausible Mechanism

The possible mechanism for the RATRP of MMA initiated with TPM/$CuCl_2$/PMDETA is proposed in Scheme 1.



Scheme 1. Plausible initiation mechanism of RATRP of MMA initiated with TPM/CuCl$_2$/ PMDETA.

The C-H bond of TPM is easy to dissociate to generate two radicals, Tr· and H· (Eq 1 in Scheme 1). This was proved by the addition of 2,2-diphenyl-1-picrylhydrazhyl (DPPH). When DPPH was added to the CHO solution of TPM at 80°C, the red color disappeared quickly.

These two radicals can either initiate the polymerization, but they should experience different processes. For Tr·, it should undergo a normal RATRP mechanism (Eq 2). It is noteworthy that Tr· may also act as an "iniferter", nevertheless, this should not affect the mechanism, which is similar to those reported by Qiu et al [11-14]. As for H·, if it undergo this mechanism (Eq 3), the homolysis of HCl should be rather difficult. In addition, if HCl is constantly generated, it may destroy the complex of the basic ligand PMDETA. Therefore, this reaction should be insignificant. Consequentially, H· should firstly add to the double bond of MMA, resulting in the monomer radical, M·, which then build the equilibrium of active and dormant species (Eq 4 and 5). Nevertheless, as we mentioned above, owing to the high activity, H·may undergo many side reactions, such as radical termination, transfer, disproportionation and so on.

Conclusions

The RATRP of MMA initiated by TPM in the presence of CuCl2/PMDETA was successfully conducted. The polymerization exhibited the characteristics of living/controlled polymerization, that is, first-order kinetics with respect to monomer, linear increase of M_n relative to conversion and low PDI. The omega-Cl can be utilized to prepare block copolymer. Effect of solvent demonstrates that the polymerization is absolutely solvent-dependent. Moreover, other factors such as temperature and feed ratio were also discussed. Finally, the mechanism was proposed. The polymerization should be initiated by two different radical generated by thermal cleavage of TPM, however, the polymerization proceed in a controlled manner.

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