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Nitroxide-mediated polymerization of methyl methacrylate by 4,4'-dimethoxydiphenyl-based alkoxyamine†

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Nitroxide-mediated polymerization of methyl methacrylate (MMA) was carried out using 4,4'dimethoxydiphenyl nitroxide-based alkoxyamine as a mediator. This alkoxyamine can be easily prepared and is able to control the nitroxide-mediated polymerization of MMA up to a conversion of 65%. A linear increase of the number-average molecular weight with conversion was observed and polymers with narrow molecular weight distributions (PDI = 1.2-1.4) were obtained. The living character was also confirmed by chain extension from the prepared poly(methyl methacrylate) macroinitiator with MMA or styrene. ESR (electron spin resonance) results indicate that the living chain fraction is more than 85%. Additionally, the MMA polymerization cannot be well controlled by the diphenylnitroxide-based alkoxyamine because of the unwanted cross combination reaction between two nitroxides; the prepared polymer shows a bimodal and broad molecular weight distribution.

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Introduction

Nitroxide-mediated polymerization (NMP) is a powerful technique to prepare well-defined (co)polymers with controllable molar masses, narrow molar mass distribution and end group functionalities.¹⁻⁶ NMP operates by the reversible trapping of growing polymer chains with nitroxides and is controlled by the so-called persistent radical effect which was established by Fischer and Fukuda.^{7,8} Compared with other controlled/living radical polymerization (CLRP) techniques like atom transfer radical polymerization (ATRP)9 and reversible additionfragmentation chain transfer (RAFT),10 NMP has always been considered as a more simple method due to a simple control system, a thermal activation mechanism and no purifications for the polymer except simple precipitation to remove unreacted monomer. 2,2,6,6-Tetramethyl-1-piperidinyloxy nitroxide (TEMPO) was first successfully used to control the polymerization of styrene.11,12 Now, a variety of nitroxides with different structures have been introduced in NMP to extend the range of monomers,13-16 while methyl methacrylate (MMA) is still a challenging one.17,18 A big breakthrough was made by Guillaneuf et al. who utilized 2,2-diphenyl-3-phenylimino-2,3dihydroindol-1-yloxyl (DPAIO)-based alkoxyamines as a mediator for NMP.19 Because the presence of a phenyl ring allows the delocalization of free radical, the cross-disproportionation of

nitroxide with propagating macroradicals would be minimized. Grubbs et al. developed a methodology based on the addition of C-centered radicals obtained from alkyl halides precursors to nitroso to prepare the corresponding N-phenyl alkoxyamines compounds, and moderate control at low monomer conversion was obtained with this alkoxyamines.20,21 Several sterically hindered imidazoline nitroxides and their corresponding alkoxyamines bearing a spiro cyclic moiety were prepared by Edeleva et al. Although the good control was achieved up to a conversion of about 55%, the synthesis of alkoxyamines is complicated.²² Yoshida investigated the photo-living radical polymerization of MMA mediated by TEMPO using a photo-acid bis(alkylphenyl)iodonium hexafluorophosphate generator, (BAI), PMMA with a narrow molecular weight distribution was produced but the mechanism remained unclear as the role of the BAI was not elucidated.23,24

Until now, the use of diarylnitroxides as control radicals in NMP has been seldom studied. Being different from nitroxides usually used in NMP, the stability of these radicals is generally attributed to electron delocalization. Diphenylnitroxide (DPN) was the first diarylnitroxide reported by Wieland *et al.*²⁵ But the use of DPN in NMP is restricted because of the high electron density on the carbon atom in *para*-position, this would cause a cross combination reaction (Scheme 1). Haghighat and coworkers have utilized DPN to control the polymerization of 1,3-butadiene, while a bimodal molecular weight distribution of the final product was observed.²⁶ This is ascribed to the dimerization reaction occurred during the oxidation process of aromatic diphenylamine. 4,4'-Dimethoxydiphenyl nitroxide (DMDPN) was later synthesized by Meyer *et al.*²⁷ The presence of methoxy groups in *para* position of phenyl rings makes DMDPN

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Scheme 1 Instability of the diphenylnitroxide.

much more stable than its parent radical DPN. Considering the high stability, simple preparation, and delocalization effect of DMDPN, we intended to investigate the capability of DMDPN and its corresponding alkoxyamine in the controlling radical polymerization of MMA.

Experimental

Materials

4,4'-Dimethoxydiphenyl amine (99%), potassium peroxymonosulfate (oxone, 99%), tetra-*n*-butylammonium hydrogen sulfate (99%), ethyl 2-bromoisobutyrate (99%), and PMDETA (99%) were purchased from J&K Chemical Reagent and used as received. Potassium hydroxide (KOH, >96%), methylene chloride (CH₂Cl₂, 99%), acetone (99%), ethanol (99%), acetonitrile (MeCN, 99%), ethyl acetate (99%), and hexane (99%) were purchased from Sinopharm Chemical Reagent (SCRC, Shanghai, China) and used as received. 2,2'-Azobis(isobutyronitrile) (AIBN, 98%) was purchased from SCRC and purified by recrystallization in ethanol. MMA and styrene were purchased from SCRC and distilled before use. Glass tubes (custom-built, length = 400 mm, inner diameter = 4 mm, outer diameter = 6 mm) were used in polymer synthesis.

Characterization

¹H NMR spectra were recorded on a Bruker Avance 300M NMR spectrometer using deuterated chloroform as the solvent and tetramethylsilane as the reference. The pH value was probed by a pH-meter (LEICI PHS-2C) with a micro-pH electrode (E201-4). The average molecular weight and molecular weight distribution of polymers were measured at 30 °C using a Waters 1525/ 2414 gel permeation chromatography (GPC) system (Waters, Milford) equipped with PLgel 10 μ m columns (500 Å, 10³ and 10^4) (molecular weight ranges: 100 to 800 000 g mol⁻¹) and refractive index detector. Poly(methyl methacrylate)s with narrow molecular weight distributions were used as standards $(M_{\rm p}/{\rm PDI}$ of the standards: 645/1.29, 1970/1.10, 5000/1.09, 10 900/1.04, 27 600/1.02, 60 150/1.03, 138 600/1.02, 298 900/ 1.02, 625 500/1.03, 1 677 000/1.08). THF was used as the eluent at a flow rate of 1 mL min⁻¹. Electron spin resonance (ESR) experiments were carried out on a Bruker A300 spectrometer.

Synthesis of 4,4'-dimethoxydiphenyl nitroxide

Acetone (80 mL), CH_2Cl_2 (60 mL), tetra-*n*-butyl ammonium hydrogen sulfate (0.085 g, 0.25 mmol), phosphate buffer

(60 mL), and 4,4'-dimethoxydiphenyl amine (0.9160 g, 4 mmol) were added into a 250 mL flask and stirred vigorously at 0 °C. A solution of oxone (10 g, 16.3 mmol) in water (90 mL) was then added to the mixture drop-wise over a period of 1 h. The pH of reaction mixture was monitored by a pH-meter and kept constant at pH 7.5–8 by adding 2 mol L^{-1} solution of KOH. The reaction mixture became deep red within several minutes. Upon completion of the addition, the reaction was allowed to proceed at 0 °C for 2 h under stirring. The CH₂Cl₂ layer was separated and the aqueous phase was extracted with CH2Cl2 for three times. The organic phase was dried with anhydrous MgSO4 and concentrated by vacuum distillation. The crude product was purified by silica gel column chromatography (hexane : ethyl acetate = 3:1). The nitroxide (0.83 g, yield = 85%) was obtained as red crystals. Anal. calc. for C14H14NO3: C, 68.85%; H, 5.74%; N, 5.74%. Found: C, 68.53%; H, 6.01%; N, 5.69%.

Synthesis of ethyl 2-((bis(4-methoxyphenyl)amino)oxy)-2methylpropanoate

DMDPN (1.32 g, 5.4 mmol), copper powder (0.172 g, 2.5 mmol), ethyl 2-bromoisobutyrate (0.98 mg, 5 mmol) and MeCN (10 mL) were added into a 25 mL flask and stirred under continuous stirring. The flask was sealed with a rubber septum, placed in an oil bath at 30 °C, and degassed by bubbling with argon for 20 min. PMDETA (0.5 g, 3 mmol) was added by syringe. After 3 h, the mixture was diluted by 100 mL of ethyl acetate, and washed with 10% HCl, saturated NaHCO₃, and saturated NaCl, respectively. The organic phase was dried with anhydrous MgSO₄ and concentrated by vacuum distillation. The crude product was purified by silica gel column chromatography (hexane : ethyl acetate = 5 : 1). The alkoxyamine (1.69 g, yield =87%) was light red crystals. ¹H NMR: δ 1.30 (t, 3H; CH₃-CH₂O), δ 1.50 (s, 6H; CH₃), δ 3.77 (s, 6H; O-CH₃), δ 4.17 (s, 2H; CH₂), δ 6.83 (d, 4H; Ar-H), δ 6.67 (d, 4H; Ar-H); anal. calc. for C₂₀H₂₅NO₅: C, 70.19%; H, 6.96%; N, 3.90%. Found: C, 69.98%; H, 7.08%; N, 4.02%.

Typical polymerization experiment

MMA (20 g, 0.2 mol) and alkoxyamine (0.18 g, 0.5 mmol) were mixed and stirred until the alkoxyamine was fully dissolved. The solution was then degassed by N_2 bubbling for 20 min and added into several glass tubes. The tubes were sealed and placed into a preheated oil bath at 110 °C. After polymerization for a certain period, the tube was removed from the oil bath and immersed into ice-water to stop the reaction. The polymer was isolated by precipitating the reaction mixture into cold ethanol. Conversion was determined gravimetrically. The average molecular weight and polydispersity index were determined by GPC.

Chain extension polymerization

Chain extension polymerization initiated by a DMDPN-capped PMMA macroinitiator was conducted for both MMA and styrene. The DMDPN-capped PMMA macroinitiator was precipitated in methanol twice before use. For the MMA chain extension, the macroinitiator was dissolved in MMA (1000 equiv.) and allowed to react at 110 $^{\circ}$ C for 3 h. For the styrene chain extension, the macroinitiator was dissolved in styrene (4000 equiv.) and allowed to react at 125 $^{\circ}$ C for 6 h.

Results and discussion

DMDPN was synthesized according to the method reported by Brik.²⁸ The synthetic route of DMDPN-based alkoxyamine is illustrated in Scheme 2. 4,4'-Dimethoxydiphenyl amine was oxidized to DMDPN by oxone under biphasic conditions (CH_2Cl_2/H_2O) rapidly; this reaction showed high yield (85%) after 3 h. The alkoxyamine was prepared using the reported method of Harrisson.²⁹ Ethyl 2-bromoisobutyrate was used to generate the corresponding alkyl radicals in this study.

A series of polymerization experiments were conducted under different conditions to study the controllability of DMDPN and its alkoxyamine to control the polymerization of MMA (Table 1). In a preliminary study, we conducted the polymerization of MMA with DMDPN under a bimolecular initiating system using AIBN as initiator at 110 °C (entry 1, Fig. 1). When the DMDPN/AIBN feed ratio is 1.6 and the targeted M_n is 80 kg mol⁻¹, a large discrepancy was observed between the theoretical and calculated molecular weights. The PDIs were higher than 1.8 at different conversions, which is above the limit of controlled polymerization. However, the plots of ln[M]₀/[M] *vs.* time and molecular weight (M_n) *vs.* conversion were linear which have shown promise in controlling MMA polymerization with DMDPN. The poor controllability over MMA polymerization under bimolecular initiating system was also reported by Guillaneuf for DPAIO/PERKADOX 16 (bis(*tert*-butylcyclohexyl)peroxydicarbonate) pair.¹⁹ Because the unimolecular system generally have better controllability over molecular weight and polydispersity than the bimolecular initiating system,³⁰ DMDPN-based alkoxyamine was then used as a mediator in the MMA polymerization.

As displayed in Table 1, when the DMDPN-based alkoxyamine was used, 39% conversion was achieved in 9 h (entry 2). The measured molecular weights can be well fit by the theoretical ones and the molecular weight distributions were narrow under different monomer/alkoxyamine ratios; this suggests a "living" character of this polymerization (entries 2 and 3). The $\ln[M]_0/[M]$ vs. time and molecular weight vs. conversion plots are shown in Fig. 2. The kinetic plot was pseudo-first-order and the molecular weight increased linearly with conversion up to a conversion of about 65% (Fig. 2a). The measured molecular weights were consistent well with the theoretical values and the PDIs were small at different conversions (Fig. 2b). The polymerization was also conducted at 90 °C (entry 4); it proceeded quite slowly at this temperature and the origin of the linear correlation did not go through 0 (Fig. 2a). The measured molecular weights were higher than the theoretical values; the PDIs were relatively large but still smaller than 1.5 (Fig. 2b). This decreased controllability may be due to the slow initiation rate of the alkoxyamine at 90 °C.

Chain extension polymerization of MMA initiated by the DMDPN-capped PMMA macroinitiator was conducted to check the living character. To prepare the DMDPN-capped PMMA macroinitiator, the bulk MMA polymerization reaction at 110 °C was stopped and quenched at a conversion of 13%; the polymer was purified by precipitation in methanol twice ($M_n = 5200 \text{ g mol}^{-1}$, PDI = 1.25). 1 g of the macroinitiator was dissolved in 19.25 g of MMA monomer (1000 equiv.) and allowed to react at 110 °C for 3 h. The result is shown in Fig. 3. The GPC trace shift obviously to



Scheme 2 Synthesis of DMDPN-based alkoxyamine.

Table 1 Summary of experimental conditions and results for MMA polymerization in bulk								
Entry	Initiating system	Temperature (°C)	Targeted M_n (kg mol ⁻¹)	Time (h)	Convn (%)	$M_{\rm n,GPC} \left({ m kg mol}^{-1} \right)$	$M_{\rm nth} ({\rm kg \ mol}^{-1})$	PDI^{b}
1	DMDPN/AIBN = 1.6	110	80	7	51	64.5	20.4	1.88
2	Alkoxyamine ^a	110	40	9	39	16.3	15.6	1.25
3	Alkoxyamine	110	80	10	32	27.1	25.6	1.3
4	Alkoxyamine	90	40	22	18	13.2	6.0	1.4

^a Alkoxyamine represents the DMDPN-based alkoxyamine. ^b Determined by GPC.



Fig. 1 (a) Evolution of $\ln[M]_0/[M]$ vs. time for the polymerization of MMA at 110 °C under a bimolecular initiating system. DMDPN/AIBN = 1.6, targeted $M_n = 80$ kg mol⁻¹. The solid line is the line of best fit. (b) Evolution of M_n (**D**) and PDI (**A**) vs. conversion. The dashed line corresponds to the theoretical M_n .



Fig. 2 (a) Evolution of $\ln[M]_0/[M]$ vs. time for the polymerization of MMA mediated by DMDPN-based alkoxyamine at 110 °C (**I**) or 90 °C (**O**) targeted $M_n = 40$ kg mol⁻¹. (b) Evolution of M_n (full symbol) and PDI (empty symbol) vs. conversion.

the smaller elution time, indicating that the DMDPN-capped PMMA macroinitiator had living chain ends and could be reinitiated.



Fig. 3 Chain extension polymerization of MMA initiated by the DMDPN-capped PMMA macroinitiator. Macroinitiator: $M_n = 5200 \text{ g} \text{ mol}^{-1}$, PDI = 1.25 (solid line). After polymerization for 1.5 h: $M_n = 12300 \text{ g} \text{ mol}^{-1}$, PDI = 1.31 (dashed line). After polymerization for 3 h: $M_n = 21300$, PDI = 1.35 (dotted line).

The DMDPN-capped PMMA macroinitiator was also used for the chain extension polymerization of styrene, which allows for the preparation of diblock copolymer. Considering the poor solubility of PMMA in styrene, 1 g of the macroinitiator was dissolved in 80.1 g of styrene monomer (4000 equiv.). The polymerization was conducted at a higher temperature of 125 °C to increase the conversion. The GPC curve of prepared diblock copolymer is shown in Fig. 4. As shown in this figure, when styrene was used as the second monomer, the PMMA-*b*-PS diblock copolymer with high molecular weight was prepared. Although the PDI of prepared PMMA-*b*-PS was broad (PDI = 2.21), there was no low-molecular-weight peak or shoulder in the GPC trace after precipitation. This means that nearly all the DMDPN-capped PMMA macromolecules were converted to the block copolymers.

ESR measurements were carried out to confirm the living nature of prepared DMDPN-capped PMMA. The DMDPN-capped PMMA macroinitiator, which was the same as that used in the chain extension polymerization, was dissolved in *tert*-butyl benzene to get 0.1 mmol L^{-1} solution with oxygen as the scavenger. After heating to 110 °C, the ESR spectra of DMDPN was observed and its signal increased with time (Fig. 5).



Fig. 4 Chain extension polymerization of styrene initiated by the DMDPN-capped PMMA macroinitiator. Macroinitiator: $M_n = 5200 \text{ g}$ mol⁻¹, PDI = 1.25 (solid line). After polymerization for 6 h: $M_n = 52300 \text{ g}$ mol⁻¹, PDI = 2.21 (dashed line).

After the macroinitiator was fully decomposed, the quantification of the signal showed that the concentration of the DMDPN released was $0.0856 \text{ mmol } \text{L}^{-1}$, which means that the fraction of living chains is more than 85%.

In order to assess the effect of the para-substitution on the phenyl ring on polymerization, DPN-based alkoxyamine was also synthesized in the same way and used for the polymerization of MMA (110 °C, targeted $M_n = 40 \text{ kg mol}^{-1}$). After polymerization under the same conditions, a bimodal molecular weight distribution with large PDI (>3) was observed for the prepared polymers. This bimodal distribution has been attributed to the formation of difunctional nitroxide during the oxidation process²⁶ and disappeared after a reduction treatment. The same reduction experiment of prepared PMMA was also conducted; however, no difference in GPC traces was observed (see ESI[†]), meaning that the difunctional nitroxide formation mechanism was not responsible for the poor controllability of DPN to MMA polymerization. The decomposition path way of DPN exhibited in Scheme 1 might be the main reason, in which diphenylamine and N-phenyl-p-benzoquinoimine N-oxide were formed and retarded the polymerization. This suggests that the para-substitution on the phenyl



Fig. 5 Growth of the ESR signal upon heating (T = 110 °C) of the PMMA macroinitiator ($M_n = 5200$ g mol⁻¹, PDI = 1.25), before heating (dotted line), 40 min of heating (dashed line), 5 hours of heating (solid line).

ring plays an important role in the polymerization of MMA with diarylnitroxides.

Conclusions

While most of the nitroxides used in nitroxide-mediated polymerization were dialkylnitroxides, with at least one hindered alkyl group linked to the N atom, diarylnitroxides which have different stability mechanism were seldom studied in NMP. In this work, DMDPN was synthesized by oxidation of 4,4'-dimethoxydiphenyl amine with oxone in high yield and its corresponding alkoxyamine was employed as a mediator in NMP of MMA. At 110 °C, the living polymerization of MMA up to about 65% conversion was achieved, showing the linear increase of $M_{\rm n}$ vs. conversion and the narrow molecular weight distributions (PDI = 1.20-1.4) of prepared polymers at the different monomer/alkoxyamine feed ratios. An induction period appeared when the polymerization was conducted at 90 °C, due to the slow initiation rate of alkoxyamine. The prepared DMDPN-capped PMMA could be reinitiated by MMA or styrene, which confirmed the living character of the chain ends. The diblock polymer was successfully prepared by using styrene as the second monomer in the chain extension polymerization, in spite of its relatively large PDI. The high living chain fraction was evidenced by ESR. For comparison, the diphenylnitroxidebased alkoxyamine was synthesized and used to mediate the polymerization of MMA. A bimodal molar weight distribution with PDI > 3 was observed for the prepared polymer, suggesting the importance of the para-substitution on the phenyl ring when dialkylnitroxides were used in NMP of MMA.

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