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Atom transfer radical polymerization of dimethyl(methacryloyloxymethyl) phosphonate

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ABSTRACT

Atom transfer radical polymerization (ATRP) of dimethyl(methacryloyloxymethyl) phosphonate (DMMAMP, also referred to as MAPC1) with a copper/2,2′-bipyridine based catalytic system in DMSO resulted in a homopolymer with narrow molecular weight distribution. Initiators for continuous activator regeneration (ICAR) ATRP of this monomer was also successful when using tris[(2-pyridyl)methyl]amine as ligand and azobisisobutyronitrile as supplementary initiator for the regeneration of the Cu^I activator. Normal ATRP provided better control compared to ICAR ATRP. Differential scanning calorimetry measurements of the resulting poly(DMMAMP) revealed a glass transition temperature ($T_g = 63 \,°C$), lower than that of poly(methyl methacrylate). Chain extension of the poly(dimethyl(methacryloyloxymethyl) phosphonate) macroinitiator with styrene was successfully achieved with a high fraction of block copolymer.

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1. Introduction

Phosphorus containing polymers find applications as flame-retardant additives [1–3], membranes for fuel cells [4,5], adhesives [6], hole-transporting materials in OLEDs [7], and as bio-related materials [8–10]. Dimethyl(methacryloyloxymethyl) phosphonate (DMMAMP, also referred to as MAPC1) is one of a few phosphorus containing vinyl monomers that can be radically polymerized to form polymers with the phosphorus functionality in the side chain, providing good adhesive and anticorrosive properties [11–13].

Atom transfer radical polymerization (ATRP) [14–21] is one of the most powerful reversible-deactivation radical polymerization (RDRP) techniques, and was already employed to polymerize DMMAMP [11]. However, the homopolymerization of DMMAMP by ATRP was not well controlled, and the reaction yielded a homopolymer with lower molecular weight (MW) than theoretically predicted

and broad molecular weight distribution (MWD). This could be ascribed to selection of not optimized reaction conditions, slow deactivation or excessive radical termination at early stages of the polymerization, which might be caused by inefficient deactivation of the low MW radicals [12,22–27]. A decrease in the concentration of radicals during the polymerization or selection of a catalyst with higher rate of deactivation could yield polyDMMAMP with higher MW and narrower MWD. Recently, successful reversible addition-fragmentation transfer (RAFT) homopolymerization of DMMAMP in DMF at 70 °C was reported [28,29] forming polyDMMAMP with controlled MW and narrow MWD [28].

In this paper, we present results of investigation of ATRP of DMMAMP that led to well-defined polymers (Scheme 1). Ethyl α-bromophenylacetate (EBPA) was used as the initiator with a $Cu^I Br/Cu^{II} Br_2$/bpy (2,2′-bipyridine) and TPMA (tris[(2-pyridyl)methyl]amine) catalyst systems. The resulting polyDMMAMP was thoroughly characterized by gel permeation chromatography (GPC), ^{1}H NMR spectroscopy, and differential scanning calorimetry (DSC). A polyDMMAMP-Br macroinitiator was successfully

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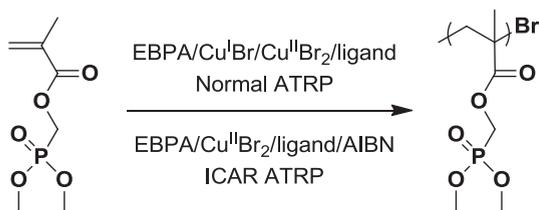
Scheme 1. Normal ATRP or ICAR ATRP of dimethyl(methacryloyloxym-ethyl) phosphonate (DMMAMP).

chain-extended with styrene (St) to provide a phosphorus-containing block copolymer.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma Aldrich unless otherwise stated. Dimethyl(methacryloyloxymeth-yl) phosphonate (DMMAMP) monomer was provided by SPECIFIC POLYMERS Inc. Copper(I) bromide (Acros, 98%) was washed with glacial acetic acid to remove any soluble oxidized species, filtered, washed twice with anhydrous ethyl ether, dried and kept under vacuum. Monomers were passed through a column of basic alumina to remove inhibitors before polymerization.

2.2. Measurements

Monomer conversion was measured using ^{1}H NMR spectroscopy (Bruker Avance 300 Hz spectrometer) in CDCl$_3$. Molecular weight (MW) and molecular weight distribution (MWD, M_w/M_n) were determined by GPC using PSS columns in DMF containing 50 mM LiBr as the eluent at a flow rate of 1 mL/min at 50 °C. The GPC system was composed of a Waters 515 HPLC Pump and Waters 2414 Refractive Index Detector. Each sample was filtered through neutral alumina prior to analysis. Differential scanning calorimetry (DSC) measurements were performed using a DSC-Q20 (TA Instruments). Thermal measurements were performed at heating and cooling rates of 10 °C/min and the reported glass transition temperatures were obtained during the second heating cycle.

2.3. Homopolymerization of DMMAMP

A normal ATRP of DMMAMP was carried out with the initial ratio of reagents of [DMMAMP]$_0$/[EBPA]$_0$/[Cu^{I}Br]$_0$/[Cu^{II}Br$_2$]$_0$/[bpy]$_0$ = 200/1/0.1/0.9/2. The DMMAMP mono-mer (2.0 g, 9.6 mmol), EBPA initiator (0.012 g, 0.048 mmol), Cu^{II}Br$_2$ (0.0096 g, 0.043 mmol), 2,2′-bipyri-dine (bpy) (0.015 g, 0.096 mmol), and 50% (v/v) DMSO were added to a 10 mL Schlenk flask equipped with a stir bar. The mixture was degassed via three freeze–pump–thaw cycles, and Cu^{I}Br (0.00069 g, 0.0048 mmol) was then added to the flask when the solution was frozen during the final cycle. The flask was sealed and placed in an oil bath at 40 °C. Samples were taken periodically under N$_2$ atmo-sphere using a N$_2$ purged syringe, diluted with DMF,

passed through a neutral alumina column to remove the copper complex, and analyzed by GPC.

An ICAR ATRP was carried out with the initial ratio of reagents in the polymerization of [DMMAMP]$_0$/[EBPA]$_0$/[Cu^{II}Br$_2$]$_0$/[TPMA]$_0$/[AIBN]$_0$ = 200/1/0.1/0.1/0.1. The DMMAMP monomer (2.0 g, 9.6 mmol), EBPA initiator (0.012 g, 0.048 mmol), Cu^{II}Br$_2$ (0.0011 g, 0.0048 mmol), tris[(2-pyri-dyl)methyl]amine (TPMA) (0.0014 g, 0.0048 mmol), and 50% (v/v) CH$_3$CN were added to a 10 mL Schlenk flask equipped with a stir bar. The mixture was degassed via three freeze–pump–thaw cycles, followed by the addition of azobis-isobutyronitrile (AIBN) (0.00079 g, 0.0048 mmol) to the frozen solution during the final cycle. The flask was sealed and placed in an oil bath at 60 °C. Samples were taken peri-odically under N$_2$ atmosphere using a N$_2$ purged syringe, diluted with DMF, passed through a neutral alumina column to remove the copper complex, and analyzed by GPC.

2.4. Synthesis of polyDMMAMP-block-polySt

A sample of polyDMMAMP-Br macroinitiator, formed by a normal ATRP of DMMAMP under the above conditions, was precipitated by adding the solution to tetrahydrofuran (THF). The precipitate was separated, redissolved in MeOH and reprecipitated into THF three more times. The result-ing polyDMMAMP-Br macroinitiator was dried under vac-uum at room temperature for 24 h and analyzed by GPC employing linear PMMA standards and ^{1}H NMR spectros-copy in CDCl$_3$, indicating that the polyDMMAMP-Br had a $M_n = 2.08 \times 10^4$, and $M_w/M_n = 1.22$.

The polyDMMAMP-Br macroinitiator was used for the ATRP of styrene with the initial ratio of reagents of [St]$_0$/[polyDMMAMP]$_0$/[Cu^{I}Br]$_0$/[PMDETA]$_0$ = 1000/1/1/1 at 100 °C in 50% (v/v) DMSO. Styrene (1.0 g, 9.6 mmol), poly-DMMAMP-Br (0.20 g, 0.0096 mmol), N,N,N′,N′,N″-penta-methyldiethylenetriamine (PMDETA) [30] (0.0017 g, 0.0096 mmol), and 50% (v/v) DMSO were added to a 10 mL Schlenk flask equipped with a stir bar. The mixture was degassed via three freeze–pump–thaw cycles, and Cu^{I}Br (0.0014 g, 0.0096 mmol) was added to the reaction mixture when the solution was frozen during the final cycle. The flask was sealed and placed in an oil bath at 100 °C. The polymer-ization was stopped after 24 h by cooling the flask to room temperature and opening the flask to air. The solution was purified by passing it through a column of neutral alumina to remove the copper complex, and analyzed by GPC. The resulting polymer was precipitated by adding the solution to methanol. The precipitate was separated, redissolved in THF and reprecipitated into same solvent three times. The final polymer was dried under vacuum at room tempera-ture for 24 h and analyzed by GPC.

3. Results and discussion

3.1. Normal ATRP of DMMAMP

Conditions for a normal ATRP of DMMAMP were inves-tigated by changing the initial ratio of [DMMAMP]$_0$/[EBPA]$_0$/[Cu^{I}Br]$_0$/[Cu^{II}Br$_2$]$_0$/[ligand]$_0$ and at different tem-peratures in 50% (v/v) DMSO and the results are provided

in Table 1. When PMDETA (pentamethyldiethylenetriamine) was employed as the ligand with the ratio of $[DMMAMP]_0/[EBPA]_0/[Cu^IBr]_0/[Cu^{II}Br_2]_0/[PMDETA]_0 = 200/1/0.5/0.5/1$ at 60 °C (Table 1, P1), monomer conversion reached 25% within 1 h. However, the polymerization did not proceed beyond 1 h, remaining at ca. 25% conversion until 18 h. This result could be attributed to a significant termination at the beginning of polymerization. This can be ascribed to the higher ATRP equilibrium constant ($K_{ATRP} = k_{act}/k_{deact}$) in DMSO, compared to a nonpolar solvent, and the initially too low concentration of the Cu^{II} deactivator [31–42], resulting in higher radical concentration and enhanced radical termination reactions.

Bpy was selected as the ligand for the normal ATRP in order to decrease the rate of polymerization of DMMAMP, due to relatively lower K_{ATRP} with bpy compared to PMDETA, which should reduce the radical concentration [43–45]. However, as shown in Table 1, entry P2, with the ratio of $[DMMAMP]_0/[EBPA]_0/[Cu^IBr]_0/[Cu^{II}Br_2]_0/[bpy]_0 = 200/1/0.5/0.5/2$ in 50% (v/v) DMSO at 60 °C, the polymerization was not well controlled, generating a polymer with lower molecular weight than theoretical and with a broad MWD ($M_w/M_n > 1.6$), although conversion reached 84% after 2 h. When ATRP of methyl methacrylate (MMA) was carried out under the same conditions, conversion only reached 4.0% after 72 h (Table 1, M1). The faster polymerization of DMMAMP could be attributed to a significantly larger K_{ATRP} or larger propagation rate coefficient (k_p) in the polymerization of DMMAMP than that of MMA, although the latter is less likely, according to a small alkyl group effect on k_p for methacrylate monomers [46]. The GPC traces of the sample in DMF showed a tailing towards the lower MW region. The resulting polymer was precipitated into THF and analyzed by ^1H NMR spectroscopy. The spectrum confirmed the presence of peaks attributable to the protons from –CH$_3$ and –CH$_2$– groups around the phosphorus.

One challenge in ATRP of DMMAMP is the possible coordination of copper species by phosphonate groups. Therefore, the ligand strongly complexing Cu was selected and optimization of the polymerization conditions was conducted. The effect of adding $Cu^{II}Br_2$ to reduce the initial radical concentration was examined with the initial ratio of reagents $[Cu^IBr]_0/[Cu^{II}Br_2]_0 = 0.1/0.9$ at 60 °C in 50% (v/v) DMSO, (Table 1, P3). The polymerization was better controlled, generating a homopolymer with relatively narrow MWD ($M_w/M_n = 1.35$). When the reaction temperature was decreased, the MWD was even narrower (Table 1, P4)

and the number-average MW (M_n) was closer to the theoretical value (Fig. 1(a)). As shown in Fig. 1(b), the peaks in GPC traces shifted toward higher MW region with increasing reaction time and the traces displayed less tailing.

3.2. ICAR ATRP of DMMAMP

Initiator for continuous activator regeneration (ICAR) ATRP of DMMAMP was examined because ICAR ATRP enables the rate of polymerization to be controlled in the presence of a low concentration of copper by addition of a thermal radical initiator to generate and, then regenerate the Cu^I activator, e.g., AIBN [47,48]. ICAR ATRP of DMMAMP was carried out with three types of ligand and a ratio of $[DMMAMP]_0/[EBPA]_0/[Cu^{II}Br_2]_0/[ligand]_0/[AIBN]_0 = 200/1/0.1/0.1/0.1$, with PMDETA or TPMA as ligand, and a ratio of $200/1/0.1/0.2/0.1$ with bpy, at 60 °C in 50% (v/v) CH$_3$CN. The results are listed in Table 2. The polymerizations were not well-controlled when using PMDETA or bpy as ligands (Table 2, P5 and P6) and polymers displayed broad MWD. On the other hand, as shown in Fig. 1(c), ICAR ATRP using TPMA as the ligand was well controlled, providing polymers with relatively narrow MWD below ca. 30% conversion. According to a previous report, a degree of control of ICAR ATRP depends on the value of K_{ATRP}, correlated with a stability of the $Cu^{II}Br_2$/ligand complex [47]. The $Cu^{II}Br_2$/TPMA complex exhibits a higher stability, resulting in a higher concentration of deactivator. However, as the polymerization with TPMA ligand proceeded, the M_n deviated from theoretical values (Table 2, P7), and the GPC trace had observable tailing (Fig. 1(d)), indicating presence of chain breaking reactions with increasing conversion [25,49].

3.3. Chain extension from polyDMMAMP-Br macroinitiator with styrene

The polyDMMAMP-Br macroinitiator was chain extended with St in a normal ATRP with the ratio of $[St]_0/[polyDMMAMP-Br]_0/[Cu^IBr]_0/[PMDETA]_0 = 1000/1/1/1$ at 100 °C in 50% (v/v) DMSO. The copolymerization reached 20% conversion after 24 h, forming a polyDMMAMP-block-polySt copolymer. The GPC traces showed that the initial macroinitiator was almost fully chain-extended, generating a new population of polyDMMAMP-block-polySt copolymer chains (Fig. 2) with $M_w/M_n = 1.58$. This result indicates that polyDMMAMP-Br macroinitiator, prepared via ATRP under these conditions

Table 1
Normal ATRP of DMMAMP (P1 ~ P4) or MMA (M1) in 50% (v/v) DMSO.

Entry	$[M]_0/[I]_0/[Cu^IBr]_0/[Cu^{II}Br_2]_0/[ligand]_0$	Ligand	Temp.(°C)	Time (h)	Conv.(%)[a]	$M_{n,exp}$[b]	$M_{n,theo}$[c]	M_w/M_n[b]
P1	200/1/0.5/0.5/1	PMDETA	60	1	25	23,400	10,400	1.36
				18	26	19,600	10,800	1.47
P2	200/1/0.5/0.5/2	bpy	60	2	84	22,300	35,000	1.60
P3	200/1/0.1/0.9/2	bpy	60	4	80	21,300	33,300	1.35
P4	200/1/0.1/0.9/2	bpy	40	8	65	21,700	27,100	1.22
M1	200/1/0.5/0.5/2	bpy	60	72	4.0	Not determined		

M = monomer. I = EBPA initiator.
[a] Conversion was measured by ^1H NMR.
[b] $M_{n,exp}$ and M_w/M_n were obtained from GPC in DMF using PMMA standard.
[c] $M_{n,theo}$ was calculated based on conversion measured by ^1H NMR. $[DMMAMP]_0 = 3.0$ M; $[MMA]_0 = 6.2$ M; 50% DMSO by volume.
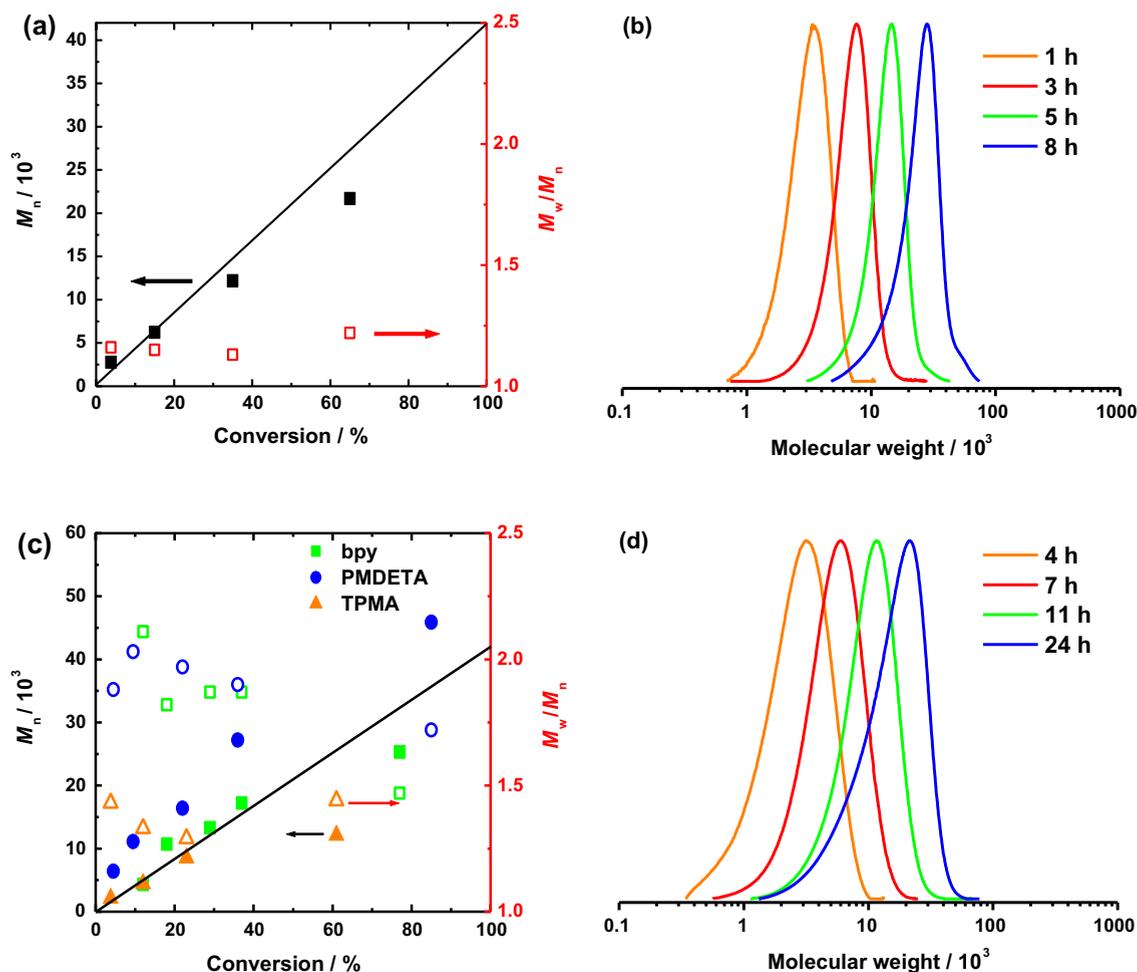
Fig. 1. Normal and ICAR ATRP of DMMAMP. (a) Plot of M_n and M_w/M_n *vs.* conversion and (b) GPC traces in DMF using PMMA standards with $[DMMAMP]_0/$
$[EBPA]_0/[Cu^IBr]_0/[Cu^{II}Br_2]_0/[bpy]_0 = 200/1/0.1/0.9/2$; $[DMMAMP]_0 = 3.0$ M in 50% (v/v) DMSO at 40 °C. (c) Plots of number average MW (M_n) and dispersity
index (M_w/M_n) *vs.* conversion with $[DMMAMP]_0/[EBPA]_0/[Cu^{II}Br_2]_0/[ligand]_0/[AIBN]_0 = 200/1/0.1/0.1/0.1$ (ligand = PMDETA and TPMA) or $200/1/0.1/0.2/0.1$
(ligand = bpy); $[DMMAMP]_0 = 3.0$ M in 50% (v/v) CH_3CN at 60 °C and (d) GPC traces in DMF using PMMA standards with $[DMMAMP]_0/[EBPA]_0/[Cu^{II}Br_2]_0/$
$[TPMA]_0/[AIBN]_0 = 200/1/0.1/0.1/0.1$; $[DMMAMP]_0 = 3.0$ M in 50% (v/v) CH_3CN at 60 °C. The black line indicates theoretical line.

Table 2
ICAR ATRP of DMMAMP in 50% (v/v) CH_3CN using AIBN.

Entry	$[M]_0/[I]_0/[Cu^{II}Br_2]_0/[ligand]_0/[AIBN]_0$	Ligand	Temp. (°C)	Time (h)	Conv. (%)[a]	$M_{n,exp}$[b]	$M_{n,theo}$[c]	M_w/M_n[b]
P5	200/1/0.1/0.1/0.1	bpy	60	24	77	25,300	32,100	1.47
P6	200/1/0.1/0.2/0.1	PMDETA	60	24	85	45,900	35,400	1.72
P7	200/1/0.1/0.1/0.1	TPMA	60	24	61	12,100	25,400	1.44

M = monomer. I = EBPA initiator.
[a] Conversion was measured by ^{1}H NMR.
[b] $M_{n,exp}$ and M_w/M_n were obtained from GPC in DMF using PMMA standards.
[c] $M_{n,theo}$ was calculated based on conversion measured by ^{1}H NMR. $[DMMAMP]_0 = 3.0$ M; 50% CH_3CN by volume.

and relatively limited MW, preserved high chain end
functionality.

3.4. Glass transition temperature of polyDMMAMP

The polyDMMAMP homopolymer prepared by normal
ATRP (P4) was purified by passing through a neutral
alumina column to remove catalyst and subsequent

precipitation into THF to remove unreacted monomer,
providing a polymer with a $M_n = 22,000$. Characterization
by DSC indicated that the glass transition temperature of
the polyDMMAMP was $T_g = 63$ °C, lower than that of
polyMMA. The decrease in T_g compared to PMMA can
be attributed to the plasticizing effect of the
phosphonate groups along the polymer backbone
[50,51].

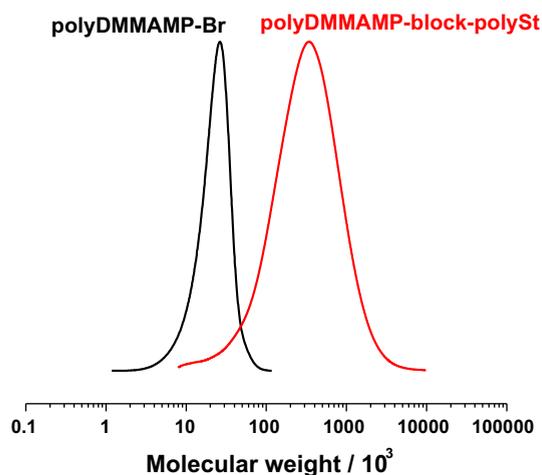**polyDMMAMP-Br**   **polyDMMAMP-block-polySt**

Fig. 2. GPC traces of polyDMMAMP macroinitiator (black line) and polyDMMAMP-block-polySt copolymer (red line) in DMF eluent using PMMA standards. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Conclusion

Both, a normal and an ICAR ATRP of DMMAMP were successful, providing homopolymers with high MW and relatively narrow MWD. Normal ATRP resulted in a better controlled process than ICAR ATRP. The resulting poly-DMMAMP homopolymers showed a lower T_g than poly-MMA. An ATRP chain extension of the polyDMMAMP-Br macroinitiator with St yielded a well-defined polyDMM-AMP-block-polySt copolymer, confirming that ATRP had produced a polyDMMAMP with controlled MW and well-preserved chain end functionality. The discussed procedures allow the synthesis of well-defined functional phosphorus-containing polymeric materials.

Acknowledgments

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