# Articles

## Atom Transfer Radical Polymerization of Dimethyl(1-ethoxycarbonyl)vinyl Phosphate and Corresponding Block Copolymers

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ABSTRACT: Atom transfer radical polymerization (ATRP) of dimethyl(1-ethoxycarbonyl)vinyl phosphate (DECVP) was investigated in the presence of different catalyst systems and initiators. Polymers with controlled molecular weight and relatively low polydispersity (PDI < 1.5) were obtained through ATRP initiated with ethyl 2-bromoisobutyrate (EBriBu) in the presence of Cu(I)Cl/2,2′-bipyridine (bpy). Faster polymerization and higher monomer conversion were obtained in the polymerization using Cu(I)Cl/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) or Cu(I)Cl/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as the catalyst system. PDECVP dissolves in water below 70 °C, but its lower critical solution temperature (LCST) depends on the polymer concentration. The conversion of PDECVP to poly((1-ethoxycarbonyl)vinylphosphonic diacid) (PECVPD) was accomplished by reaction with bromotrimethylsilane followed by methanolysis. Block copolymers, PDECVP-*b*-poly(styrene) (PS), PDECVP-*b*-PS-*b*-PDECVP, and PDECVP-*b*-poly(methyl methacrylate) (PMMA), were synthesized by extending from PS−Br, Br−PS−Br, and PMMA−Br macroinitiators. The controlled block copolymers were obtained, PDECVP-*b*-PS with $M_n$ = 40 500 g/mol and PDI = 1.4, PDECVP-*b*-PS-*b*-PDECVP with $M_n$ = 41 500 g/mol and PDI = 1.23, and PDECVP-*b*-PMMA with $M_n$ = 29 700 g/mol and PDI = 1.08. Initiation efficiency exceeded 94% using PMMA−Br as the macroinitiator.

### Introduction

Phosphorus-containing polymers are involved in a large range of applications. For example, they have been used as adhesion promoters for paints, lacquers, and adhesives,[1] flame-retardant additives,[2] complexing agents to recover metal ions from the environment and industrial liquids,[3] and agents for controlling crystallization of $CaCO_3$[4] and also have been proposed for use in tissue engineering and drug controlled release because of their biocompatibility and biodegradability.[5,6]

One of the methods of incorporating phosphorus functionality into polymers is the polymerization or copolymerization of phosphorus-containing vinyl monomers such as vinyl and allyl phosphonates.[7,8] Another approach to phosphorus-containing polymers is simple modification of polymers with phosphorus-containing groups, such as those obtained through the phosphorylation of poly(vinyl alcohol), cellulose, and polydienes.[9] Polymers with phosphorus in the backbone are usually synthesized by either polycondensation or ring-opening methods.[5,10] Atom transfer radical polymerization (ATRP),[11] one of the most robust controlled/living radical polymerization (CRP) techniques, allows for the controlled polymerization of various monomers such as styrenes,[12] acrylates,[13] methacrylates,[14,15] acrylamides,[16] and acrylonitrile.[17] It is interesting to explore the possibility for preparation of organophosphorus polymers via this method. For this investigation, we selected for our studies dimethyl(1-ethoxycarbonyl)vinyl phosphate (DECVP), a monomer that not only contains the weakly electron-donating phosphonate functional group but also electron-withdrawing ethoxycarbonyl group and may possess a captodative (cd) structure. The resulting polymer is very attractive with two types of functional groups introduced into the same polymer chain, providing a material with unique properties.

In this paper, homopolymerization of DECVP and preparation of block copolymers with S and MMA via ATRP are discussed. Consisting of a hydrophilic PDECVP segment and a hydrophobic segment, these amphiphilic block copolymers are capable of forming polymeric associates in aqueous solutions via self-assembly and can be potentially used in drug delivery or tissue engineering.

Moreover, the temperature sensitivity of PDECVP aqueous solutions has been examined via turbidity measurements. The conversion of PDECVP to poly((1-ethoxycarbonyl)vinylphosphoric diacid) (PECVPD) has also been investigated.

### Experimental Section

**Materials.** All chemicals were obtained from Aldrich unless otherwise stated. Styrene (S) (99%) and methyl methacrylate (MMA) (98%) were vacuum-distilled before use. Cu(I)Br and Cu(I)Cl were purified by stirring in glacial acetic acid overnight, filtering, and washing with dry ethanol. Tris(2-di-

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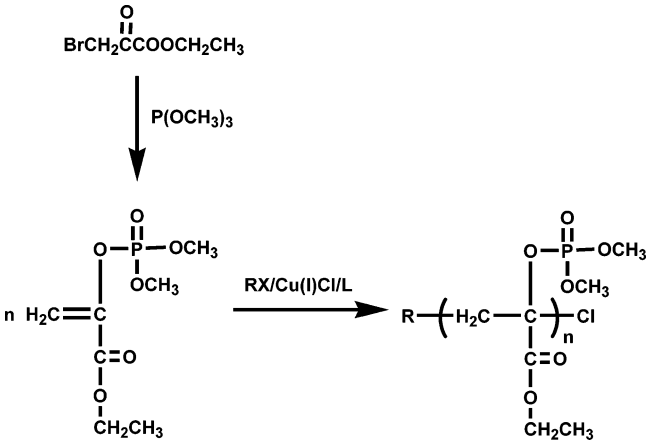
**Scheme 1. ATRP of DECVP**




methylaminoethyl)amine ($Me_6$TREN) was prepared from TREN by a procedure similar to that of Ciampolini and Nardi.[18] Trimethyl phosphate (99%), 2,2′-bipyridine (bpy) (99%), ethyl bromopyruvate (90%), *p*-toluenesulfonyl chloride (*p*TsCl) (99%), $Cu(II)Cl_2$, $CuBr_2$, *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) (99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (97%), dimethyl 2,6-dibromoheptanedioate (DMDBHD) (97%), bromotrimethylsilane (97%), 2-butanone (99%), and ethyl 2-bromoisobutyrate (EBriBu) (98%) were used without further purification.

**Measurements.** Monomer conversion of MMA and S was determined using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector using a J&W Scientific 30 m DB WAX Megabore column. Injector and detector temperatures were kept constant at 250 °C with a heating rate of 20 °C/min. Molar masses and molar mass distributions were measured on a GPC system consisting of a Waters 510 HPLC pump, three Waters UltraStyragel columns (500, $10^3$, and $10^5$ Å), and a Waters 410 DRI detector, with a DMF flow rate of 1.0 mL/min; poly(methyl methacrylate) and polystyrene were used as standards.

A PC-controlled Perkin-Elmer Lambda 900 UV/vis/NIR spectrophotometer was used to assess the cloud points of aqueous solutions of PDECVP. A solution of the polymer (4 mL, 1% w/v) was transferred to a tube equipped with a UV probe. The polymer solution was heated from 25 to 90 °C at a heating rate of 1 °C/min. The change of the transmittance was monitored as a function of temperature at a fixed wavelength of 500 nm.

$^1$H NMR characterization was performed in $CDCl_3$ and $D_2O$ on a Bruker 300 MHz instrument.

**Monomer Synthesis.** DECVP was synthesized in a manner similar to that described by Barton et al. (Scheme 1).[19] Trimethyl phosphate (31 g, 0.25 mol) was added dropwise to a stirred solution of ethyl bromopyruvate (49 g, 0.25 mol) at 0 °C under argon. The reaction mixture was stirred at room temperature for 1 h and then at 50 °C for 2 h. The product was isolated by distillation at 80−85 °C, 1 mmHg (90% yield). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 1.33 (t, 3H, $J$ = 7.1 Hz), 3.86 (d, 6H, $J$ = 11.4 Hz), 4.29 (q, 2H, $J$ = 7.1 Hz), 5.62 (t, 1H, $J$ = 2.6 Hz), 5.98 (t, 1H, $J$ = 2.4). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 14, 54.9, 61.9, 110.8, 143.6, 161.6.

**Homopolymerization of DECVP.** A typical ATRP was carried out as follows: in a 10 mL dried Schlenk flask, DECVP (1 g, 4.5 mmol), EBriBu (6.7 $\mu$L, 0.045 mmol), and 2-butanone (1 mL) were added. After three freeze−pump−thaw cycles, bpy (14.1 mg, 0.09 mmol) and Cu(I)Cl (4.4 mg, 0.045 mmol) were added under $N_2$. After stirring for 10 min at room temperature (rt), the flask was placed in a thermostated oil bath at 70 °C. Samples were taken to analyze the monomer conversion by $^1$H NMR and molecular weight by GPC in different time intervals during the polymerization. The polymerization was stopped by cooling to room temperature and opening the flask to air. The mixture was then dissolved in 10 mL of acetone and passed through neutral alumina column. The final pure product was obtained after precipitating in hexanes.

**Synthesis of Bromo-Terminated (PMMA−Br) Macroinitiator.** To a dry 100 mL Schlenk flask, MMA (10 g, 0.1 mol), PMDETA (29 $\mu$L, 0.14 mmol), and anisole (10 mL) were charged. After three freeze−pump−thaw cycles, Cu(I)Br (18 mg, 0.125 mmol) and $Cu(II)Br_2$ (2.8 mg, 0.0125 mmol) were added under $N_2$. The mixture was stirred for 10 min at room temperature before injecting EBriBu (36 $\mu$L, 0.25 mmol) and then immersed in an oil bath at 70 °C to start polymerization. The samples were drawn during the course of polymerization and diluted with THF. One portion of the solution was used for gas chromatograph (GC) to determine the monomer conversion; the remaining portion was used for GPC analysis. The polymer was purified using the same procedure as that described in the DECVP homopolymerization section.

**Synthesis of Bromo-Terminated Monofunctional Polystyrene (PS−Br) Macroinitiator.** The same procedure as that used for synthesis of PMMA−Br macroinitiator was utilized.

**Synthesis of Bromo-Terminated Difunctional Macroinitiators (Br−PS−Br)**. The same procedure as that used for synthesis of PS−Br macroinitiator was utilized except that DMDBHD was used as the initiator.

**Synthesis of PMMA−PDECVP Block Copolymers.** To a dry 10 mL Schlenk flask PMMA−Br, macroinitiator (0.7 g, 0.028 mmol), DECVP (2.4 g, 11.0 mmol), and 2-butanone (2.2 mL) were charged. After three freeze−pump−thaw cycles, the Cu(I)Cl (2.8 mg, 0.028 mmol) and bpy (9.0 mg, 0.056 mmol) were added under $N_2$. The mixture was stirred for 10 min at room temperature before being immersed in an oil bath at 70 °C to start polymerization. Samples were taken to analyze monomer conversion by $^1$H NMR and molecular weight by GPC at different time intervals during the polymerization. The polymer was purified using the same procedure as that described in the DECVP homopolymerization section.

**Preparation of Poly((1-ethoxycarbonyl)vinylphosphonic diacid) (PECVPD).** Into a 10 mL round-bottom flask, 0.5 g (2.2 mmol phosphate group) of PDECVP (entry 5, Table 1) and 5 mL of $CH_2Cl_2$ were introduced. After complete dissolving of PDECVP, 1.6 mL (10.4 mmol) of $BrSi(CH_3)_3$ was added in a dropwise manner, and the mixture was stirred at room temperature for 12 h. Then, solvent and volatile residues were evaporated. The methanolysis of the silylated intermediate was realized by adding an excess of methanol (5 mL). The mixture was stirred at room temperature for 12 h, and the solvent was evaporated. A slightly yellowish powder was quantitatively obtained after washing with ether.

## Results and Discussion

**Polymerization of DECVP.** The presence of electron-withdrawing and -donating substituents in DECVP was expected to stabilize the radicals during ATRP. This could lead to fast ATRP and low initiation efficiency. Therefore, the combination of reactive initiators and less active catalysts was originally selected. ATRP of DECVP using *p*-toluenesulfonyl chloride (*p*TsCl)[14,20] as the initiator and Cu(I)Cl/2,2′-bipyridine (bpy) as the catalyst was performed in 50 vol % 2-butanone at 70 °C (entry 1, Table 1). After more than 15 h, no polymerization occurred. Decreasing the concentration of catalyst in the system (entry 2, Table 1) or the temperature (entry 3, Table 1) did not induce polymerization. Interestingly, after styrene (60 mol %) was introduced to the reaction mixture of entry 1, polymerization occurred, and the molecular weights increased with monomer conversion. Peaks for both S and DECVP units were observed in the $^1$H NMR spectrum of the resulting polymer (not shown). The content of S in the copolymer is 62% based on integral areas of DECVP and S in the $^1$H NMR spectrum and agreement with their tendency for alternation in copolymerization reported in the literature.[8]

**Table 1. Results for ATRP of DECVP[a]**

| entry | $[RX]_0/[M]_0/[Cu(I)Cl]_0/[L]_0/[Cu(II)Cl_2]_0$ | RX | L | time (h) | conv (%) | $M_n$ (g/mol) expt | $M_n$ (g/mol) theor | PDI |
|---|---|---|---|---|---|---|---|---|
| 1 | 1/100/1/2 | *p*TsCl | bpy | 15 | 0 | | | |
| | addition of S ($V_S/V_{DECVP}$ = 1:1) | | | 2 | 15 | 2800 | 2500 | 1.6 |
| | | | | 5 | 30 | 6200 | 5400 | 1.8 |
| 2 | 1/100/0.2/0.4 | *p*TsCl | bpy | 16 | 0 | | | |
| 3 | 1/100/1/2 | *p*TsCl | bpy | 10 | 0 | | | |
| 4 | 1/100/1/2 | EBriBu | bpy | 0.7 | 10 | 3600 | 2200 | 1.38 |
| | | | | 1.9 | 15 | 5100 | 3400 | 1.40 |
| | | | | 8 | 26 | 7000 | 5800 | 1.50 |
| 5 | 1/100/1/2.1/0.1 | EBriBu | bpy | 20 | 15 | 4300 | 3400 | 1.52 |
| 6 | 1/100/1/1.1/0.1 | EBriBu | PMDETA | 0.1 | 10 | 5000 | 2200 | 1.87 |
| | | | | 0.5 | 21 | 6000 | 4700 | 1.87 |
| | | | | 2.2 | 32 | 7100 | 7200 | 1.89 |
| | | | | 6 | 46 | 9700 | 10 300 | 1.89 |
| 7 | 1/100/1/1.1/0.1 | EBriBu | HMTETA | 10 | 31 | 4900 | 6900 | 1.72 |
| 8 | 1/100/1/1 | EBriBu | HMTETA | 6 | 65 | 19400 | 14500 | 1.60 |
| 9 | 1/100/1/2 | EBriBu | $Me_6$TREN | 10 | 0 | | | |

[a] *p*TsCl = *p*-toluenesulfonyl chloride, EBriBu = ethyl 2-bromoisobutyrate, bpy = 2,2′-bipyridine, PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, HMTETA = 1,1,4,7,10,10-hexamethyltriethylenetetramine, $Me_6$TREN = tris(2-dimethylaminoethyl)amine, solvent = 2-butanone, $V_{DECVP}$:$V_{2-butanone}$ = 1:1, reaction temperature = 70 °C (25 °C for entries 3 and 9), PMMA as the GPC standard.

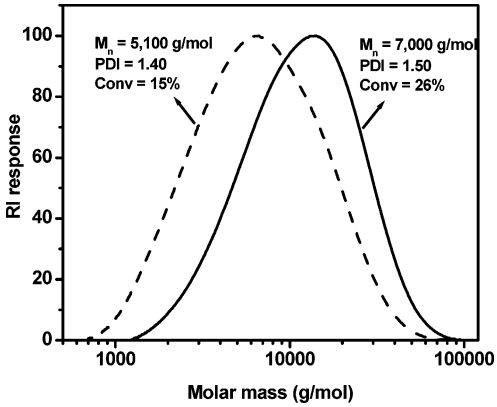



**Figure 1.** GPC traces of PDECVP prepared in the presence of EBriBu/Cu(I)Cl/bpy (entry 4, Table 1): $[EBriBu]_0$ = 44 mM; $[DECVP]_0$ = 4.4 M; $[Cu(I)Cl]_0$ = 44 mM; $[bpy]_0$ = 88 Mm, $V_{anisole}/V_{DECVP}$ = 1:1.

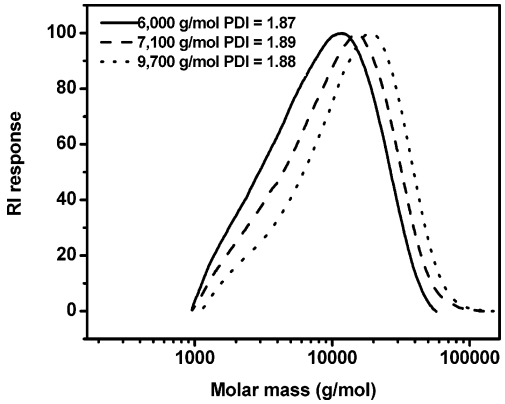



**Figure 2.** GPC traces of PDECVP in the presence of EBriBu/Cu(I)Cl/Cu(II)Cl/PMDETA (entry 6, Table 1): $[EBriBu]_0$ = 44 mM; $[DECVP]_0$ = 4.4 M; $[Cu(I)Cl]_0$ = 44 mM; $[Cu(II)Cl_2]_0$ = 0.4 mM; $[PMDETA]_0$ = 45 mM, $V_{2-butanone}/V_{DECVP}$ = 1:1.

These results suggest that addition of sulfonyl radicals to DECVP monomer at the initiation step was not efficient.

Controlled polymerization of DECVP was observed for polymerization employing ethyl 2-bromoisobutyrate (EBriBu) and Cu(I)Cl/bpy as the initiator and catalyst, respectively (entry 4, Table 1). The final polymer had a relatively narrow molecular weight distribution (PDI < 1.5). The increase of molecular weight with conversion (Figure 1) and relatively good agreement between the experimental and theoretical values demonstrate the controlled characteristic of this polymerization. However, the polymerization was fast initially, reaching 15% monomer conversion in 1.9 h, but the rate subsequently decreased. A similar phenomenon was reported in the polymerization of *tert*-butyl methacrylate in the presence of EBriBu and Cu(I)Br/ *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as the initiator and catalyst, respectively.[21] This phenomenon could be due to significant termination in the early stages of polymerization. To decrease the radical concentration and reduce termination reactions of radicals at the beginning of polymerization, $Cu(II)Cl_2$ (10 mol % of Cu(I)Cl) was added initially to serve as the deactivator (entry 5, Table 1). However, no improvement of the control over polymerization was observed, but the polymerization rate decreased significantly, as revealed by only 15% monomer conversion after 20 h. Therefore, termination reactions at the beginning of polymerization could not be the only reason for the limited monomer conversion in this polymerization. Another possible reason is that copper ion could complex with the phosphonate group through the phosphoryl oxygen.[22] The formation of a complex between copper ion and monomer/polymer could remove the copper ion from the original ligand and slow or even stop the polymerization. More studies on this complex behavior are under way.

The catalytic activity of ligands for ATRP generally increases in the following order: bipyridine < multidentate amines (e.g., PMDETA) < tripodal amines (e.g., $Me_6$TREN) < some cyclic amines ($Me_4$Cyclam).[23] Indeed, using PMDETA as the ligand[24] (entry 6, Table 1), the polymerization rate dramatically increased in comparison with the polymerization in the presence of Cu(I)-Cl/bpy. The monomer conversion reached 46% within 6 h. This increase could be due to the higher catalytic activity of the Cu(I)/PMDETA catalyst system. However, a broader molecular weight distribution (PDI = 1.8−1.9) was observed due to the slower deactivation of PMDETA catalyst system as compared with bpy. Some control of this polymerization was observed, as demonstrated by the molecular weights increasing with the monomer conversion (Figure 2). At the beginning of the polymerization, experimental molecular weights were

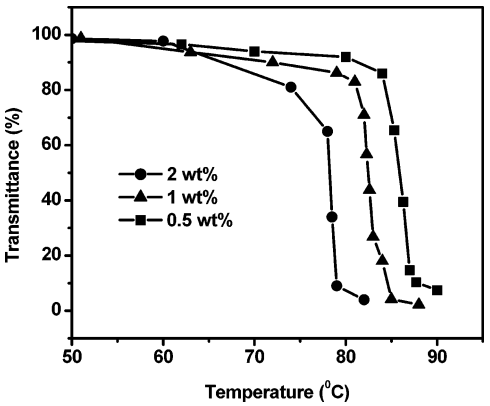



**Figure 3.** Effect of aqueous PDECVP solution concentrations on transmittance changes as a function of temperature; $M_n$ = 19 400 g/mol, PDI = 1.60.

higher than the theoretical ones, but as the polymerization progressed, they approached the theoretical values. This indicates slow initiation at early stages of the polymerization.

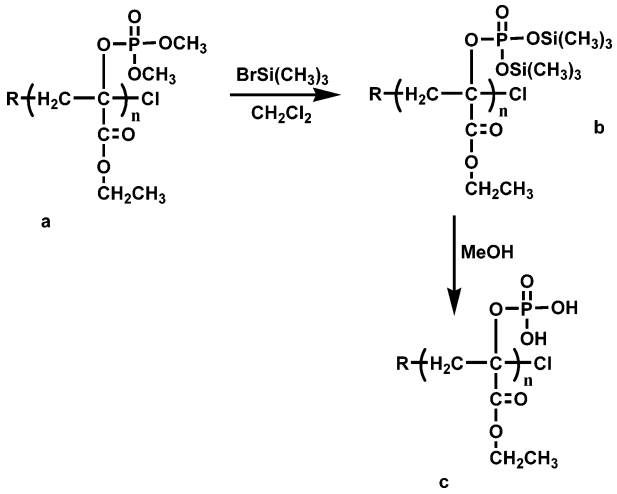
Polymerization in the presence of HMTETA was slower than that with PMDETA as ligand. The monomer conversion reached 31% after 10 h (entry 7, Table 1). However, the polymerization rate increased dramatically in the absence of $Cu(II)Cl_2$ deactivator, as indicated by 65% monomer conversion within 6 h (entry 8, Table 1).

At present, $Cu(I)/Me_6TREN$ is known to be one of the most powerful ATRP catalysts, e.g., allowing for rapid polymerization of acrylates at room temperatures even when used at very low concentrations.[25] Herein, it was used for the polymerization of DECVP in the presence of EBriBu as the initiator at room temperature (entry 9, Table 1). The color of the reaction mixture turned from light green to black green at the beginning of reaction, suggesting termination and formation of deactivator. However, even after 10 h, no polymerization occurred. This indicates that high concentration deactivator produced by the significant termination at the onset of polymerization strongly shifted the equilibrium of activation and deactivation to the dormant species side and suppressed polymerization.[26]

**Solution Properties of PDECVP.** PDECVP has phosphonate side groups, which can provide limited water solubility of the polymer. Some water-soluble polymers exhibit heat-induced phase separation in aqueous solutions,[27] the temperature of which is referred to as the critical solution temperature (CST).

The thermoresponsive solubility of the PDECVP in water was determined using a temperature-controlled UV−vis−NIR spectrometer. A series of aqueous polymer solutions with different concentrations were prepared. The polymer solution was heated at the rate of 1 °C/min, and the change of transmittance with temperature was monitored through a UV probe (Figure 3). When the LCST was reached, the transmittance decreased dramatically. This suggests that PDECVP switches from hydrophilic to hydrophobic at the transition temperature, leading to an opaque system and a significant decrease of transmittance. The transition temperatures exhibit strong dependence on the solution concentration. For example, in the case of the polymer with $M_n$ = 19 400 (g/mol) (entry 8, Table 1), it was found that the transition temperature midpoint decreased from 85 to 77 °C as the concentration increased from 0.5 to 2% (w/v).

**Scheme 2. Conversion of PDECVP to PECVPD**




**Synthesis of PECVPD.** As shown in Scheme 2, the conversion of the $-P(O)(OCH_3)_2$ functional group in PDECVP to the phosphonic diacid function group $-P(O)(OH)_2$ was carried out in a two-step sequence involving a reaction between PDECVP (**a**) and $BrSi(CH_3)_3$ followed by methanolysis. With a dropwise addition of $BrSi(CH_3)_3$ to PDECVP (**a**) in $CH_2Cl_2$, a complete reaction was observed by $^1H$ NMR, leading to silylated ester intermediate (**b**).[28] At this stage, the $^1H$ NMR spectrum (not shown) showed the absence of the broad peak at 3.8 ppm, corresponding to the protons from $-P(O)(OCH_3)_2$ in the polymer, and the presence of a singlet at 0.3 ppm, corresponding to the protons from $-Si(CH_3)_3$ groups. An excess of methanol led to the methanolysis of the silylated intermediate to provide PECVPD (**c**) in quantitative yield. The $^1H$ NMR ($D_2O$) spectrum of PECVPD (**c**) shows the absence of peak at 3.8 ppm in comparison with that of PDECVP (**a**) (Figure 4). However, because of proton exchange with the solvent, the acidic protons were not observed. To further verify the conversion of phosphonate groups of PDECVP to phosphonic diacid groups, FTIR spectra of PDECVP (**a**) and methanolysis product (**c**) were also collected. As shown in Figure 5, in contrast to the spectrum of PDECVP, a new peak appearing at 2400 $cm^{-1}$ was observed in the spectrum of product (**c**), which is attributed to OH stretch in phosphonic acid group. Meanwhile, the intensity of the peak at 1050 $cm^{-1}$ corresponding to P−O−C stretch of $P(OCH_3)_2$ function group decreases dramatically due to this functionalization.[29]

**Synthesis of S/DECVP Block Copolymers**. PS−Br has been successfully used as a macroinitiator in synthesizing different kinds of block copolymers by ATRP.[30] Well-defined PS−Br macroinitiator ($M_n$ = 18 200 and $M_w/M_n$ = 1.15), prepared in the presence of EBriBu/Cu(I)Br/Cu(II)Br/PMDETA (entry 1, Table 2), was used to initiate the ATRP of DECVP. The polymerization was carried out in the presence of Cu(I)Cl/bpy as the catalyst at 90 °C (entry 2, Table 2).

The clear shift of the SEC peak to the higher molecular weight region (Figure 6) indicates the successful block copolymerization. However, there is a shoulder remaining at the low molecular weight region, indicating that propagation was faster than initiation in this polymerization. For an efficient ATRP process, initiation should be at least as fast as propagation.

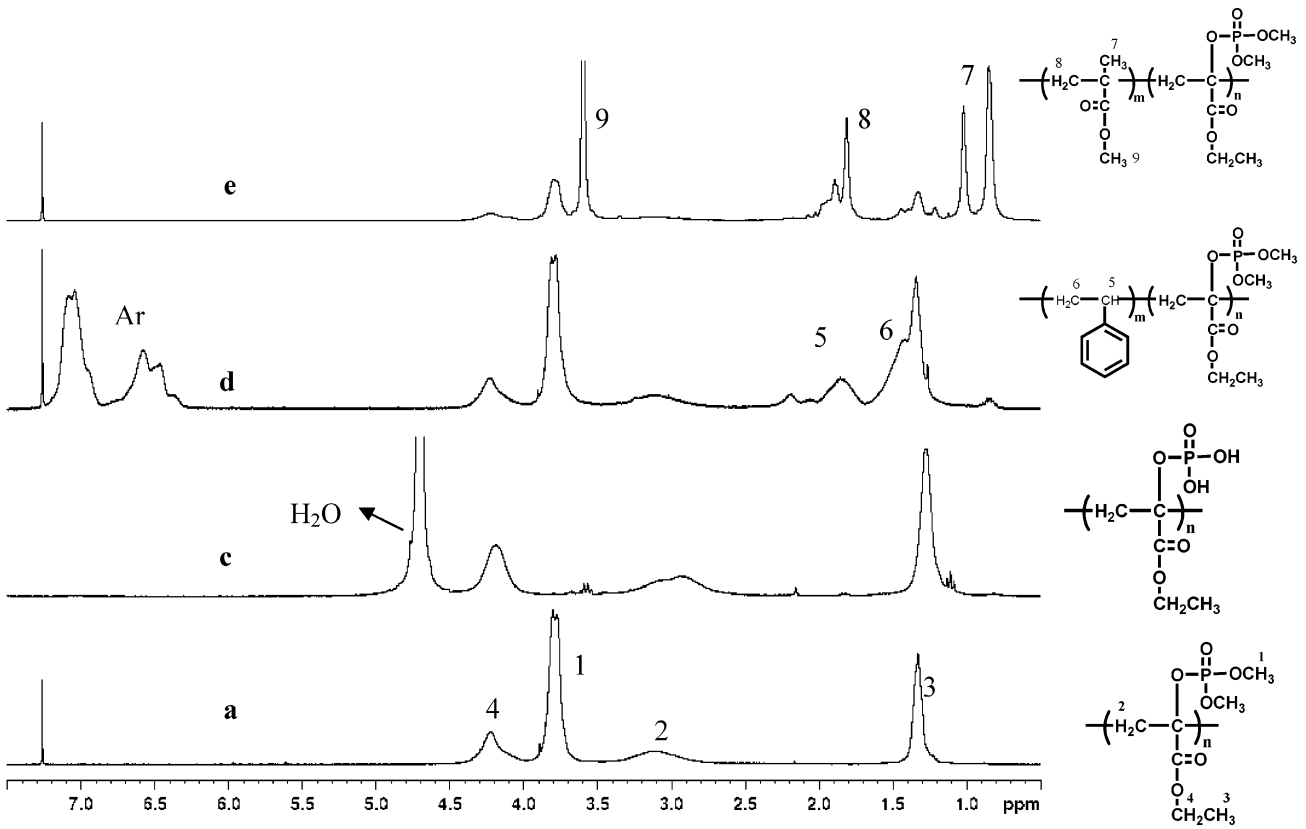



**Figure 4.** $^1$H NMR spectra of PDECVP (a) in $CDCl_3$, PECVPD (c) in $D_2O$, PDECVP−PS block copolymer (d) in $CDCl_3$, and PDECVP−PMMA block copolymer (e) in $CDCl_3$.

**Table 2. Results for Synthesis of PS−Br, Br−PS−Br, and PMMA−Br Macroinitiators and Their Corresponding Block Copolymers with DECVP[a]**

| | | | | | | $M_n$ (g/mol) | | |
|---|---|---|---|---|---|---|---|---|
| entry | $[I]_0/[M]_0/[Cu(I)X]_0/[L]_0/[Cu(II)X]_0$ | solvent (vol %) | $T$ (°C) | time (h) | conv (%) | expt | theor | PDI |
| 1 | EBriBu/S/Cu(I)Br/PMDETA/Cu(II)Br 1/400/1/1.1/0.05 | | 90 | 6 | 40 | 18 200 | 16 600 | 1.15 |
| 2 | Br-Macro.1/DECVP/Cu(I)Cl/bpy 1/850/1/2 | 50 | 90 | 20 | 13 | 40 500 | 43 000 | 1.40 |
| 3 | DMDBHD/S/Cu(I)Br/PMDETA/Cu(II)Br 1/400/1/1.1/0.05 | | 90 | 4 | 37 | 17 300 | 15 400 | 1.10 |
| 4 | Br− Macro.3-Br/DECVP/Cu(I)Cl/bpy 1/400/1/2 | 50 | 90 | 9 | 32 | 41 500 | 46 000 | 1.23 |
| 5 | EBriBu/MMA/Cu(I)Br/PMDETA/Cu(II)Br 1/400/0.5/0.6/0.05 | 50 | 70 | 5.5 | 58 | 25 500 | 23 000 | 1.20 |
| 6 | Br-Macro.5/DECVP/Cu(I)Cl/bpy 1/400/1/2 | 50 | 70 | 2.5 | 7 | 29 700 | 31 700 | 1.08 |

[a] EBriBu = ethyl 2-bromoisobutyrate, DMDBHD = dimethyl 2,6-dibromoheptanedioate, PMDETA = *N,N,N′,N″,N‴*-pentamethyldiethylenetriamine, bpy = 2,2′-bipyridine. Solvent: anisole for entry 5 or 2-butanone for others. PS as the GPC standard for entries 1 and 3, PMMA for others.

PDECVP-*b*-PS-*b*-PDECVP triblock copolymers were also obtained by extending from Br−PS−Br macroinitiator under the reaction conditions similar to those in the previous experiments (entry 4, Table 2). Initiation efficiency was improved compared with diblock copolymerization extending from PS−Br as shown by a smaller tailing in the low molecular weight region of its SEC trace (Figure 7).

**Synthesis of PMMA−PDECVP Block Copolymers.** Well-defined PMMA−Br macroinitiator was first synthesized. EBriBu was used as the initiator for the polymerization with Cu(I)Br/PMDETA catalyst system (entry 5, Table 2). 50 vol % anisole was added to decrease the initiator and catalyst concentration. A good correlation between the theoretical (from monomer conversion measurements) and experimental (from GPC analysis) molecular weights indicates high initiation efficiency occurring in this polymerization. A block copolymer was obtained by extending PMMA−Br ($M_n$ = 25 500 g/mol, PDI = 1.20) with DECVP. The clear shift of the SEC peak of PMMA to the high molecular weight region ($M_n$ = 29 700 g/mol, PDI = 1.08) and absence of a tail at the low molecular weight side demonstrates that effective initiation has taken place (Figure 8). The initiation efficiency exceeded 94%. This is reasonable since PMMA−Br is a faster initiator than PS−Br. The higher initiation efficiency in ATRP initiated by PMMA−Br in comparison with that by EBriBu is probably due to the increased reactivity of PMMA−Br triggered by the penultimate effect.[31]

**Structural Characterizations.** The $^1$H NMR spectra of obtained block copolymers and PDECVP are listed

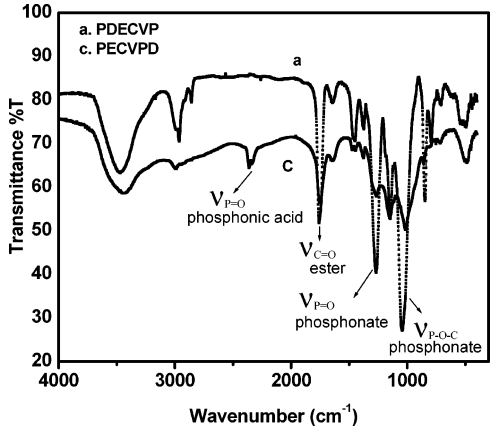



**Figure 5.** FTIR spectra of PDECVP (a) and PECVPD (c).

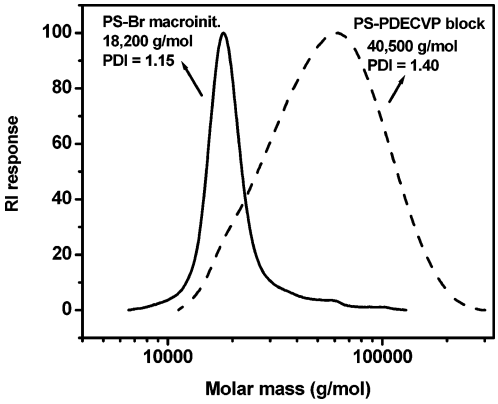



**Figure 6.** GPC traces of PS−Br macroinitiator and the PS−PDECVP block copolymer (entries 1 and 2, Table 2): $[PS-Br]_0 = 2.8$ mM; $[M]_0 = 2.4$ M; $[Cu(I)Cl]_0 = 2.8$ mM; $[bpy]_0 = 5.6$ mM, $V_{2-butanone}/V_{DECVP} = 1:1$.

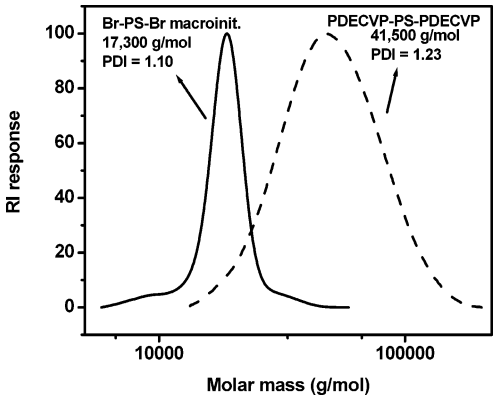



**Figure 7.** GPC traces of Br−PS−Br macroinitiator and the PDECVP−PS−PDECVP triblock copolymer (entries 3 and 4, Table 2): $[Br-PS-Br]_0 = 6.0$ mM; $[M]_0 = 2.4$ M; $[Cu(I)Cl]_0 = 6.0$ mM; $[bpy]_0 = 12.0$ mM, $V_{2-butanone}/V_{DECVP} = 1:1$.

in Figure 4. The spectrum of homo-PDECVP (**a**) contains four major resonance areas attributed to backbone methylene protons ($\delta = 2.8-3.4$ ppm, relative area = 2.0), protons of the ethyl group ($\delta = 1.2-1.4$ and 4.0−4.4 ppm, relative areas = 3.0 or 2.0), and methoxy protons ($\delta = 3.8$ ppm, relative area = 5.9). The formation of block copolymers was confirmed by comparing their $^1$H NMR spectra with that of PDECVP. In addition to the signals attributed to the protons from DECVP unit, the characteristic signals assigned to S and MMA unit are observed in the spectra of the block copolymers (Figure 4: **d**, **e**). The aromatic and methylene and methine protons from the S unit are observed at 6.3−

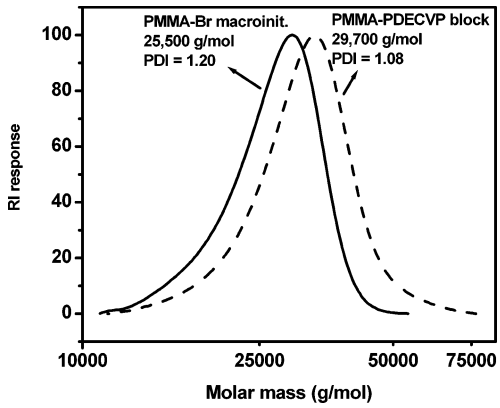



**Figure 8.** GPC traces of PMMA−Br macroinitiator and the PMMA−PDECVP block copolymer (entries 5 and 6, Table 2): $[PMMA-Br]_0 = 6.0$ mM; $[M]_0 = 2.4$ M; $[Cu(I)Cl]_0 = 6.0$ mM; $[bpy]_0 = 12.0$ mM, $V_{2-butanone}/V_{DECVP} = 1:1$.

7.2 and 1.3−2.4 ppm, respectively. The peaks at 3.6, 1.8−2.1, and 0.6−1.0 ppm correspond to protons from $OCH_3$, $CH_2$ in the backbone, and $CH_3$ of the PMMA segment. The composition of the copolymers (10 mol % DECVP), calculated according to the relative areas corresponding to protons of $-COOCH_3$ to $-PO(OCH_3)_2$, agrees with the results (~14 mol % DECVP) based on the GPC measurements.

**Conclusions.** ATRP of DECVP was carried out in the presence of different initiators and catalyst systems. Relatively controlled polymerization was accomplished when using EBriBu as the initiator and Cu(I)Cl/bpy as the catalyst. However, limited monomer conversion was reached at this polymerization condition. Switching to a more active catalyst system employing PMDETA or HMTETA led to higher monomer conversion but broader molecular weight distributions of the resulting polymers. Characterization of the solution properties of these polymers showed a strong dependence of the LCST on the polymer solution concentration. The conversion of PDECVP to PECVPD was accomplished by reacting with bromotrimethylsilane followed by methanolysis. Mono- and dibromo-functionalized PS macroinitiators were used to initiate the DECVP polymerization. Limited initiation efficiency was observed in both cases, resulting in a broader molecular weight distribution compared to macroinitiators. The PMMA−Br macroinitiator was more effective than the PS macroinitiators for initiating polymerization of DECVP, resulting in better controlled polymerizations. The characterization of the behavior of the block copolymer in solution will be described in forthcoming publications.

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