

Atom Transfer Radical Polymerization of Methyl Methacrylate Initiated with a Macroinitiator of Poly(vinyl acetate)

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ABSTRACT: Well-defined poly(vinyl acetate-*b*-methyl methacrylate) block copolymers were successfully synthesized by the atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) in *p*-xylene with CuBr as a catalyst, 2,2'-bipyridine as a ligand, and trichloromethyl-end-grouped poly(vinyl acetate) (PVAc-CCl₃) as a macroinitiator that was prepared via the telomerization of vinyl acetate with chloroform as a telogen. The block copolymers were characterized with gel permeation chromatography, Fourier transform infrared, and ¹H-NMR. The effects of the solvent and

temperature on ATRP of MMA were studied. The control over a large range of molecular weights was investigated with a high [MMA]/[PVAc-CCl₃] ratio for potential industry applications. In addition, the mechanism of the polymerization was discussed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1089–1094, 2006

Key words: atom transfer radical polymerization (ATRP); diblock copolymers

INTRODUCTION

Most block copolymers are synthesized by living polymerizations, such as anionic, cationic, organometallic,^{1,2} and group-transfer polymerizations,³ as well as 2,2,6,6-tetramethylpiperidiny-1-oxy⁴ and iniferter⁵ systems. However, with these methodologies, the synthesis of well-defined block copolymers containing a poly(vinyl acetate) (PVAc) block is still difficult, although some approaches have been reported.^{6,7} Atom transfer radical polymerization (ATRP) is a convenient way of synthesizing block copolymers because of the presence of an activated alkyl halide at a polymer chain end that can act as a macroinitiator for the subsequent block.^{8–12} Although a variety of monomers such as styrene, (meth)acrylate, and acrylonitrile have been polymerized by ATRP, ATRP of vinyl acetate (VAc), a common monomer widely used commercially, has not been successful because of its low radical reactivity. To overcome this limitation, mechanistic transformation between ATRP and conventional radical polymerization was applied to prepare poly(vinyl acetate-*b*-styrene) and poly(butyl acrylate-*b*-vinyl acetate).¹³ Difunctional initiators, azo compounds containing an activated halogen, were used. ATRP was carried before and after conventional radical po-

lymerization. The molecular distribution of the resultant copolymers ranged from 1.8 to 3.56.

Telomerization is a very convenient method for the preparation of polymers with controlled molecular weights and predetermined functionalities. When chloroform (CCl₄) is used as a transfer agent, monofunctional trichloromethylated telomers can be prepared.¹⁴ On the other hand, 1,1,1-trichloroalkanes (RCCl₃) are efficient initiators for ATRP of styrene.¹⁵ Combining these two polymerization methods (telomerization and ATRP), we prepared a well-defined block copolymer containing VAc and styrene in our laboratory.^{16(a)} ATRPs of methyl methacrylate (MMA) and methyl acrylate (MA) initiated by a VAc telomer were carried out at 90°C with CuCl/PMDETA as a catalyst system^{16(b)} in 25% (v/v) acetonitrile and 1-BuOH.

In this article, PVAc with a —CCl₃ end group and a relatively low polydispersity was synthesized by the telomerization of VAc with CCl₄. It was then used as a macroinitiator to initiate ATRP of MMA at 60°C and 80°C in a CuX (X = Cl or Br)/2,2'-bipyridine (bpy) catalyst system. The dispersity of the polymers decreased from 1.51 to 1.26, and this showed the addition of a segment with a well-defined chain length. ATRP of MMA in various solvents was studied in detail both with a high [MMA]/[PVAc-CCl₃] ratio [where PVAc-CCl₃ is trichloromethyl-end-grouped poly(vinyl acetate)] and at different temperatures for potential industry applications. A possible mechanism of the polymerization is discussed.

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EXPERIMENTAL

Materials

MMA (chemically pure; Shanghai Reagents Plant, Shanghai, China) was vacuum-distilled above CaH_2 before polymerization. VAc (analytical reagent; Shanghai Reagents Plant) was dried and distilled before use. Azobisisobutyronitrile (AIBN; analytical reagent; Shanghai Reagents Plant, Shanghai, China) was recrystallized from ethanol and vacuum-dried. CCl_4 (analytical reagent; Shanghai Reagents Plant) was distilled after heating with a 5% NaOH solution. CuCl and CuBr (analytical reagent; Shanghai Reagents Plant) were purified according to the literature.¹⁷ bpy (analytical reagent; Shanghai Reagents Plant) was recrystallized from hexane and vacuum-dried.

Synthesis of PVAc with $-\text{CCl}_3$ end groups

The general procedure was as follows: To a degassed, dry flask were added VAc, AIBN, and CCl_4 . The flask was degassed three times by freeze-pump-thaw cycles and then immersed in a water bath at 60°C . Polymerization was performed for a certain time. After dilution with methanol, the obtained polymers were precipitated in petroleum ether three times and dried *in vacuo* at 50°C for 8 h.

Synthesis of the poly(vinyl acetate-*b*-methyl methacrylate) [P(VAc-*b*-MMA)] block copolymers

To a dried flask with a magnetic bar, PVAc- CCl_3 and bpy were added and degassed, and they were followed by the introduction of CuBr and oxygen-less MMA. The mixture in the flask was degassed three times by freeze-pump-thaw cycles. The flask was put into an oil bath. At timed intervals, samples were withdrawn with a degassed syringe, first for the measurement of the monomer conversion and then for the measurements of the molecular weight and the molecular weight distribution after passing a short Al_2O_3 column.

Characterization

The monomer conversion was determined by gas chromatography. The molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC) with a Waters 150C-ALC/GPC instrument with Waters Styragel HT2 and HT4 columns and tetrahydrofuran as an eluent. Polystyrene standards were used to calibrate the columns. Fourier transform infrared (FTIR) measurements and $^1\text{H-NMR}$ characterization were performed on Nicolet Magna IR-550 spectrometer and Gemini 300 $^1\text{H-NMR}$ spectrometer, respectively.

TABLE I
Telomerization of VAc with CCl_4 Telogen
in Different Solvents

	Solvent				VAc
	Methanol	Ethanol	Benzene	Ethyl acetate	
Time t (h)	15	8	8	2	2
Conversion (%)	2.3	4.2	6.8	25.0	47.6

RESULTS AND DISCUSSION

Synthesis of macroinitiator PVAc- CCl_3 by telomerization

In industry, the radical polymerization of VAc is usually carried out in methanol. However, when CCl_4 was used as a telogen, as shown in Table I, the conversion of VAc in methanol was only 2.3% after 15 h. Therefore, the telomerization of VAc in different solvents was examined first. The results show that ethanol and benzene are also not suitable solvents because of the low polymerization rate of the monomer (Table I). In ethyl acetate and VAc bulk systems, the conversion of VAc increased. The telomerization of VAc was performed in bulk for this article. Additionally, in a bulk system, at a high conversion of monomers, an explosion of polymerization is likely because of difficulties in the transformation of heat, and the branching of polymers also can easily occur at this stage, so the conversion of VAc was controlled under 70% in the experiments.

In telomerization, according to the Mayo equation,¹⁸ the degree of polymerization (DP) can be derived as follows:

$$\frac{1}{\text{DP}} = \frac{1}{\text{DP}_0} + C_s \frac{[\text{CCl}_4]}{[\text{VAc}]} \quad (1)$$

where DP_0 is the degree of polymerization in the absence of a chain-transfer agent and C_s is the chain-transfer constant. The changes in $[\text{CCl}_4]/[\text{VAc}]$ can be neglected when the conversion of VAc is less than 5%, so $[\text{CCl}_4]/[\text{VAc}]$ at the polymerization time can be assumed to be approximately equal to the initiating $[\text{CCl}_4]_0/[\text{VAc}]_0$ ratio. Thus, under different $[\text{CCl}_4]_0/[\text{VAc}]_0$ ratios with the conversion of the monomer controlled to be less than 5%, the relation between DP and $[\text{CCl}_4]/[\text{VAc}]$ was explored according to this assumption. As plotted in Figure 1, DP of the polymers is linear to $[\text{CCl}_4]/[\text{VAc}]$, and this indicates that the molecular weight of PVAc- CCl_3 can be controlled well by $[\text{CCl}_4]/[\text{VAc}]$. According to the slope, C_s of CCl_4 in this case is 0.994. For a given ratio of the initial CCl_4 and VAc concentrations (1 : 25), VAc conversion (4.2%), and DP_0 (2273), the obtained molecular weight of the polymer was 2218 g/mol, which agreed with

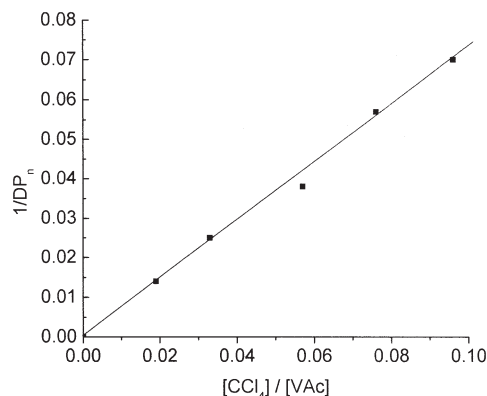


Figure 1 DP versus $[\text{CCl}_4]/[\text{VAc}]$ (temperature = 60°C, AIBN concentration = 0.04%).

the theoretical number-average molecular weight ($M_{n,\text{th}}$) of 2137 g/mol determined from eq. (1). Elemental analysis showed the concentration of chlorine atoms in the polymer was 5.6%, which was in good agreement with that in PVAc- CCl_3 .

The effect of the AIBN concentration on telomerization was studied further. Figure 2 shows that the number-average molecular weight (M_n ; ca. 3500) and weight-average molecular weight/number-average molecular weight ratio (M_w/M_n ; 1.5–1.7) of PVAc were little different with different concentrations of AIBN, and this means that the propagation of PVAc was suppressed and the polymer chain was telomerized via the strong telogen. Likewise, the length of the polymer chain tended to be identical.

Polymerization in various solvents

Unlike conventional radical polymerization, ATRP is much influenced by the medium, in which the catalysts (CuX-L) and initiators might perform in different ways. It has been reported that it is more favorable to conduct ATRP in relatively nonpolar solvents such as

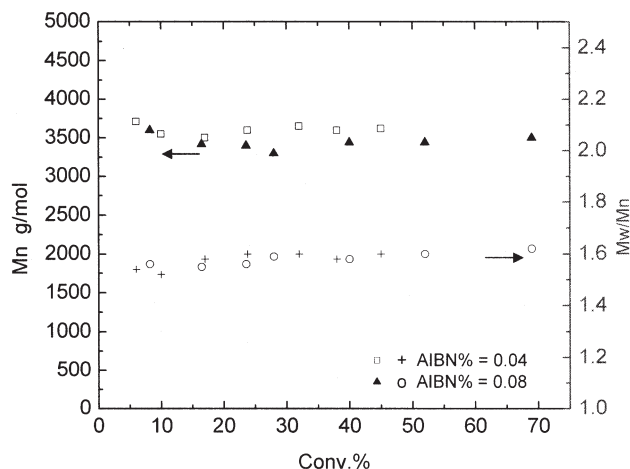


Figure 2 M_n and M_w/M_n versus the conversion ($[\text{CCl}_4]/[\text{VAc}] = 0.038$, temperature = 60°C).

benzene, *p*-dimethoxybenzene, or diphenyl ether than polar solvents.¹⁹ However, polar solvents such as ethylene carbonate, propylene carbonate, and even acetonitrile and water have been used successfully.²⁰ Therefore, ATRP showed complex properties that required more study. Among the solvents, *p*-xylene, diphenyl ether, cyclohexanone, toluene, butyl acetate, and MMA itself (in bulk) were selected for ATRP of MMA initiated with PVAc- CCl_3 in this study. The results are listed in Table II.

As shown in Table II, for the polymerization in *p*-xylene, the experimental molecular weight matches the theoretical one calculated by the ratio of the consumed monomer to the introduced macroinitiator. This suggests a good control of the molecular weight with catalysis either by CuBr-bpy or by CuCl-bpy . However, the propagation rate catalyzed by CuCl-bpy was faster than that catalyzed by CuBr-bpy . This might be due to the fact that the chlorine atom is smaller than bromine and the $\text{Cu}^{\text{II}}-\text{Cl}$ bond is stronger than the $\text{Cu}^{\text{II}}-\text{Br}$ bond;²¹ this results in a more

TABLE II
Characterization Data for ATRP of MMA in Various Solvents Catalyzed with CuBr-bpy at 80°C^a

Solvent	Reaction time (h)	Conversion (%)	M_n	M_w/M_n	$M_{n,\text{th}}$	D_e (%)
Toluene	2.5	26.3	11,200	1.45	13,000	14.0
<i>p</i> -Xylene ^b	1.0	29.5	14,700	1.35	14,200	3.7
<i>p</i> -Xylene	2.5	30	13,500	1.36	14,400	6.2
Diphenyl ether	5.0	12.3	6,270	1.50	8,100	22.7
Cyclohexanone	5.0	8.6	5,410	1.85	6,800	20.5
Butyl acetate	5.0	15.8	7,800	1.45	9,340	16.5
MMA (bulk)	0.5	62.0	18,300	1.89	25,600	28.6

^a D_e = deviation of M_n (GPC) from $M_{n,\text{th}}$.

^a $[\text{PVAc-CCl}_3]/[\text{CuBr}]/[\text{bpy}]/[\text{MMA}]_0 = 1 : 1 : 3 : 353$; $[\text{MMA}]_0 = 4.46$ mol/L; M_n (PVAc- CCl_3) = 3800 (Vapor Pressure Osmometry);

^b CuCl-bpy as the catalyst.

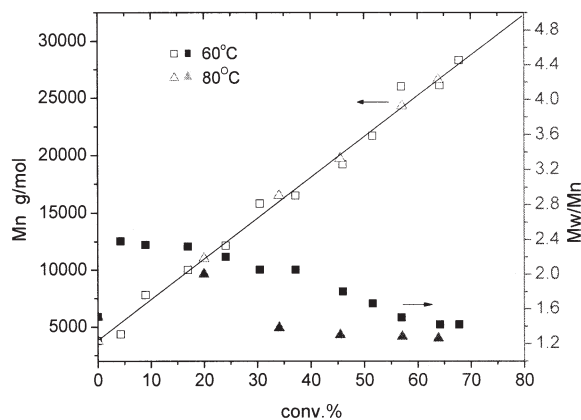


Figure 3 M_n and M_w/M_n versus the monomer conversion in ATRP of MMA ($[\text{PVAc-CCl}_3]/[\text{CuBr}]/[\text{bpy}]/[\text{MMA}]_0 = 1:1:3:353$, temperature = 60°C , $[\text{MMA}]_0 = 4.67$ mol/L in *p*-xylene).

active catalyzed center of CuCl–bpy in this system, which has more effect on the rate of the polymerization than the relative strength of the C–Br and C–Cl bonds. Table II also shows that the experimental molecular weights obtained in other solvents deviate from the theoretical values. This could be the reason for transfer and other side reactions.²⁰ The polymerization of MMA in bulk turned out to be the opposite of what we had expected, with an uncontrolled molecular weight and a broad molecular weight distribution.

Polymerization catalyzed by CuBr–bpy in *p*-xylene

According to the aforementioned results, the polymerization catalyzed by a CuBr–bpy complex in *p*-xylene preliminarily shows a living nature. This prompted us to study it in detail. For potential industry applications, emphasis was placed on the control of the polymerization over a large range of molecular weights with a high $[\text{MMA}]/[\text{PVAc-CCl}_3]$ ratio and at various temperatures in *p*-xylene. The results of the polymerization at 60 and 80°C are shown in Figures 3 and 4.

Figure 3 demonstrates that the experimental molecular weight matches well the theoretical values, and this indicates a living polymerization of MMA. The polymerization was stopped at a conversion of 68% because the reaction mixture became too viscous for the sample to be withdrawn from the flask at 60°C , a relatively low temperature. Although the molecular weight distribution becomes narrow with the MMA conversion, the polydispersities remain relatively high up to 50% conversion. This might be due to the low activation/deactivation rates between the living and dormant species at 60°C during the polymerization. At 80°C in the very early stage of the polymerization, the polydispersities soon descend below 1.5 and then as low as 1.26. Figure 3 also shows the good control of

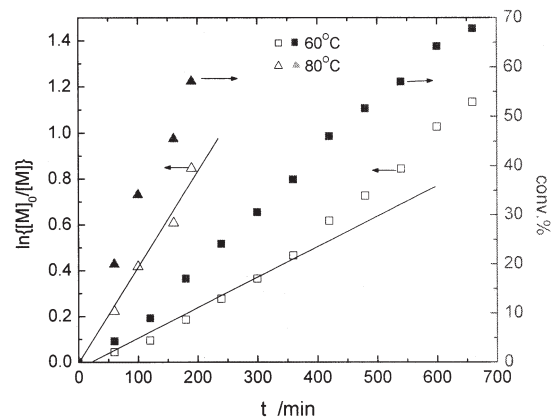


Figure 4 Kinetics plots of $\ln\{[M]_0/[M]\}$ and the conversion versus the time in ATRP of MMA ($[\text{PVAc-CCl}_3]/[\text{CuBr}]/[\text{bpy}]/[\text{MMA}]_0 = 1:1:3:353$, temperature = 60°C , $[\text{MMA}]_0 = 4.67$ mol/L in *p*-xylene).

the molecular weight as a function of the MMA conversion with the largest molecular weight as high as 28,000 as predetermined by $\Delta[\text{MMA}]/[\text{PVAc-CCl}_3]$, which could be audio-visually seen in GPC eluent curves in Figure 5. Therefore, an increase in the reaction temperature is necessary for good control of the polymerization. Figure 4 shows that the polymerization at 80°C proceeded by first-order kinetics, suggesting a constant number of living species throughout the copolymerization. However, at 60°C , when the conversion of MMA exceeded 20%, the molecular weights deviated upward from the linear plot, exhibiting a faster propagation. This indicates an increase in the concentration of the living species, presumably due to a shift of the equilibrium between the living and dormant species (Scheme 1) toward an increase in the number of living species in the viscous medium, resulting in an accelerated polymerization.

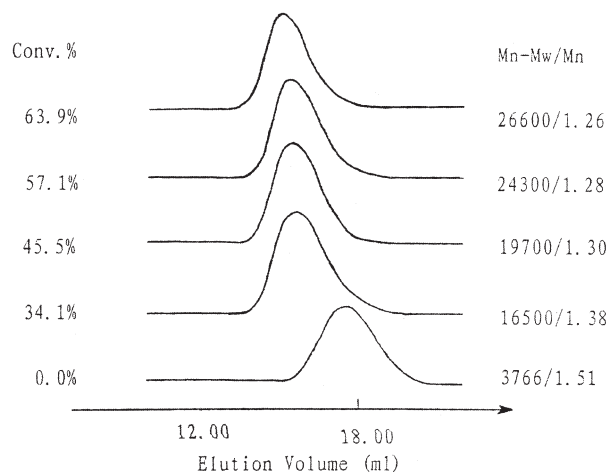
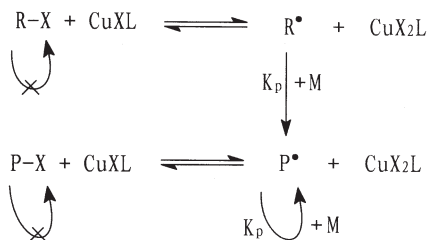


Figure 5 GPC elution curves of P(VAc-*b*-MMA) ($[\text{PVAc-CCl}_3]/[\text{CuBr}]/[\text{bpy}]/[\text{MMA}]_0 = 1:1:3:353$, temperature = 80°C , $[\text{MMA}]_0 = 4.67$ mol/L in *p*-xylene).



Scheme 1

Further investigation shows that the control of the polymerization is also much influenced by the macromolecular dimension in the polymerization of MMA in this system. Instead of the feed molar ratio of $[\text{PVAc-CCl}_3]/[\text{CuBr}]/[\text{bpy}]/[\text{MMA}] = 1:1:3:353$, with $[\text{PVAc-CCl}_3]/[\text{CuBr}]/[\text{bpy}]/[\text{MMA}] = 1:1:3:100$ at 80°C , the polymerization was controlled well with a predetermined molecular weight ($M_n = 12,000$) and a low molecular distribution ($M_w/M_n = 1.32$) up to a monomer conversion as high as 91%. This demonstrates that the proportion of chains marked by the contribution of transfer and termination increased with the chain length, being less influenced by the monomer conversion.²²

Kinetic data

The living species of ATRP seem to be radical in nature in many aspects,^{19,22} including reverse ATRP, chemoselectivities, regioselectivities, and stereoselectivities. Taking the living species as conventional radicals, we can calculate the radical concentrations at several temperatures according to the following equations:

$$R_p = -d[\text{M}]/dt = K_p[\text{M}][\text{P}^\bullet] \approx K_p^{\text{app}}[\text{M}] \quad (2)$$

$$\ln([\text{M}]_0/[\text{M}]) = K_p^{\text{app}}t \quad (3)$$

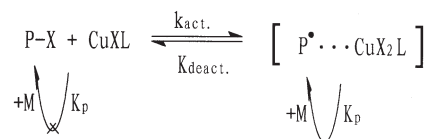
$$K_p^{\text{app}} = K_p[\text{P}^\bullet] \text{ or } [\text{P}^\bullet] = K_p^{\text{app}}/K_p \quad (4)$$

TABLE III
Kinetic Data and Estimated Concentration of Radical for ATRP of MMA in *p*-Xylene Initiated by PVAc-CCl₃ and Catalyzed by CuBr-bpy^a

	Temperature (k)			
	333	343	353	373
k_p (Ms)	788.4	996.3	1241.4	1863
k_{app} (10^4 s^{-1})	0.23	0.35	0.72	1.42
$[\text{P}^\bullet]$ (10^8 M)	2.9	3.5	5.9	7.6

^a $[\text{PVAc-CCl}_3]/[\text{CuBr}]/[\text{bpy}]/[\text{MMA}]_0 = 1:1:3:353$; 80°C ; $[\text{MMA}]_0 = 4.67 \text{ mol/L}$ in *p*-xylene.

k_p = propagating rate constant; k_{app} = apparent propagating rate constant; $[\text{P}^\bullet]$ = radical concentration.

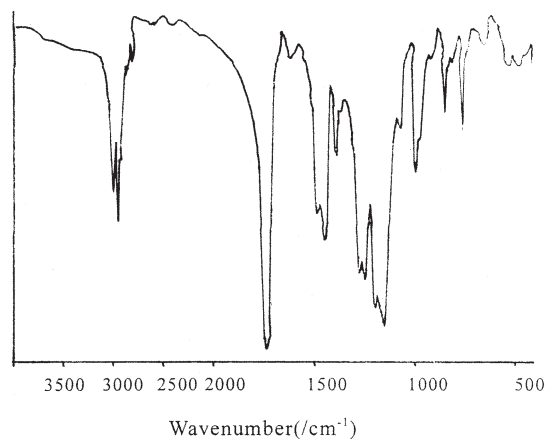


Scheme 2

where R_p , K_p , K_p^{app} , $[\text{P}^\bullet]$, $[\text{M}]_0$, and $[\text{M}]$ represent the propagating rate, propagating rate constant, apparent propagating rate constant, radical concentration, initial monomer concentration, and monomer concentration, respectively. The determined radical concentrations in combination with the kinetic data are listed in Table III.

Table III shows determined radical concentrations as high as $5.9 \times 10^{-8} \text{ mol/L}$ at 80°C , almost of the same order as that of a conventional radical polymerization system.²³ The results contradict the position of classical ATRP, which holds that it is because of the very low radical concentration, far lower than that in a conventional radical polymerization system, that the doubling termination and the disproportionation can be suppressed, leading to the controlled polymerization. The fact derived from our study suggests a complex radical nature of the living species other than a completely free radical. A suggested mechanism is shown in Scheme 2.

The complex radicals or coordinating radicals²⁴ would not easily terminate one another or disproportionate, and this would result in a living fashion of polymerization in the ATRP system. However, there are chain-breaking reactions. In the last polymerization stage, the reacting material exhibits a greenish color, which is a mixture of the brown color belonging to $\text{CuX}(\text{bpy})_2$ and the blue color belonging to $\text{CuX}_2(\text{bpy})_2$. This indicates that there must be termination and/or disproportion for the living species and coordinated radicals or free radicals decomposed from


 Figure 6 FTIR spectrum of P(VAc-*b*-MMA).

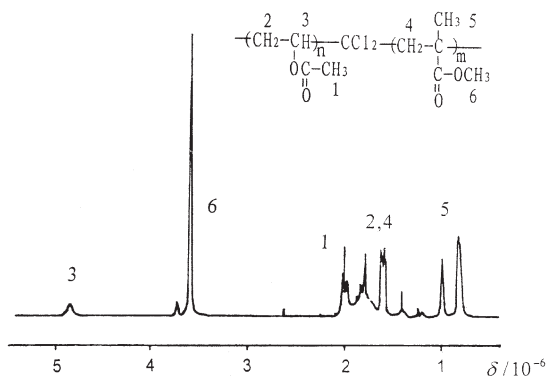


Figure 7 $^1\text{H-NMR}$ spectrum of P(VAc-*b*-MMA).

them, leading to coupling between the transient radical and the accumulation of $\text{CuX}_2(\text{bpy})_2$; this is similar to the persistent radical effect.²⁵ However, the mechanism requires study further.

Characterization of the diblock copolymer P(VAc-*b*-MMA)

As shown in Figure 6, the peak at 1730 cm^{-1} could be attributed to the carbonyl groups of the PVAc segment and/or the poly(methyl methacrylate) (PMMA) segments, so the sample was not yet confirmed to be P(VAc-*b*-MMA) by the FTIR spectrum. $^1\text{H-NMR}$ allowed the confirmation of the polymer. As shown in Figure 7, the resonance signals at $\delta = 4.8$ could be attributed to $-\text{CH}-\text{OOC}-$ of the PVAc segment. The resonance signals at $\delta = 3.5\text{--}3.8$ were attributed to $-\text{COOCH}_3$ of the PMMA segment.

CONCLUSIONS

This article demonstrates that a well-defined P(VAc-*b*-MMA) block copolymer with a broad molecular weight range can be synthesized through ATRP of MMA initiated with PVAc- CCl_3 . Efficient block copolymer formation was demonstrated by FTIR, $^1\text{H-NMR}$, and GPC. Several parameters, such as the solvents, temperature, kind of catalyst, and $[\text{PVAc-CCl}_3]/[\text{MMA}]$ molar ratio strongly influenced the control of the polymerization. The results indicate that the poly-

merization can be successfully conducted in *p*-xylene and at 80°C , catalyzed with a CuBr-bpy complex, with a largest predefined molecular weight as high as 28,000. On the basis of the kinetic data, a complex radical nature of the living species other than a completely free radical has been proposed.

References

- Szwarc, M. *Adv Polym Sci* 1983, 49, 1.
- Noshay, A.; McGrath, J. E. *Block Copolymer*; Academic: New York, 1977.
- Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbu, T. V. *J Am Chem Soc* 1983, 105, 5706.
- Kobatake, S.; Harwood, H. J.; Quirk, R. P.; Priddy, D. B. *Macromolecules* 1998, 31, 3735.
- Otsu, T.; Yoshida, M. *Makromol Chem Rapid Commun* 1982, 127, 133.
- Mardare, D.; Matyjaszewski, K. *Macromolecules* 1994, 27, 645.
- Huang, X. Y.; Lu, Z. J.; Huang, J. L. *Polymer* 1998, 39, 1369.
- Moineau, G.; Dubois, P.; Jerome, R.; Senninger, T.; Teyssie, P. *Macromolecules* 1998, 31, 545.
- Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 29, 1721.
- Matyjaszewski, K.; Timothy, E. P.; Xia, J. H. *J Am Chem Soc* 1997, 119, 674.
- Lecomte, P.; Drapier, I.; Dubois, P.; Teyssie, P.; Jerome, R. *Macromolecules* 1997, 30, 7631.
- Gaynor, S. G.; Matyjaszewski, K. *Polym Prepr* 1996, 37, 272.
- Paik, H. Y.; Teodorescu, M.; Xia, J. H.; Matyjaszewski, K. *Macromolecules* 1999, 32, 7023.
- Boutevin, B.; Macret, M.; Maubert, C.; Pietrasanta, Y.; Tanesie, M. *Tetrahedron Lett* 1978, 33, 3019.
- Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5641.
- (a) Zhang, Y. M.; Luo, N.; Ying, S. K. *China Synth Rubber Ind* 1997, 20, 314; (b) Semsarzadeh, A. M.; Mirzaei, A.; Vasheghani-Farahani, E.; Haghighi, N. M. *Eur Polym J* 2003, 39, 2193.
- Keller, R. N.; Eycoff, H. D. *Inorg Synth* 1946, 2, 1.
- Seymour, R. B. *Polymer Chemistry*; Marcel Dekker: New York, 1988.
- Wei, M.; Matyjaszewski, K. *Polym Prepr* 1997, 37, 683.
- (a) Matyjaszewski, K. *Polym Prepr* 1997, 37, 376; (b) Matyjaszewski, K. *Macromolecules* 1998, 31, 4710.
- Matyjaszewski, K.; Wang, J. L.; Grimaud, T.; Shipp, D. A. *Macromolecules* 1998, 31, 1527.
- (a) Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7572; (b) Xia, J.; Matyjaszewski, K. *Macromolecules* 1997, 30, 7692.
- Hiemenz, P. C. *Polymer Chemistry*; Marcel Dekker: New York, 1984; Section 6.
- Bellus, D. *Pure Appl Chem* 1985, 57, 1827.
- Fisher, H. *J Polym Sci Part A: Polym Chem* 1999, 37, 1885.