Synthesis of poly(vinyl acetate) block copolymers by successive RAFT and ATRP with a bromoxanthate iniferter†

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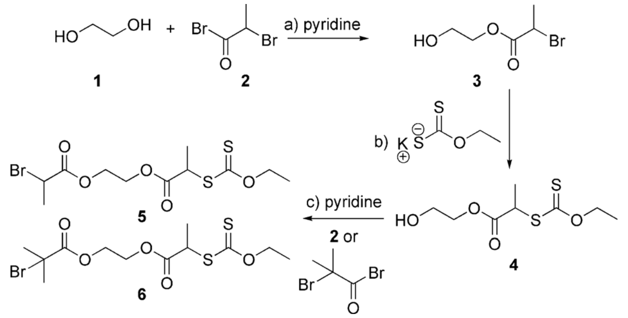
Poly(vinyl acetate)-*b*-polystyrene, poly(vinyl acetate)-*b*-poly(methyl acrylate) and poly(vinyl acetate)-*b*-poly(methyl methacrylate) block copolymers with low polydispersity (M_w/M_n < 1.25) were prepared by successive reversible addition–fragmentation chain transfer (RAFT) polymerization and atom transfer radical polymerization (ATRP) employing a bromoxanthate *iniferter* (*ini*tiator-trans*fer* agent-*ter*minator).

Block copolymers have attracted increasing attention due to their unique properties and utility in many applications.[1] Controlled radical polymerization is a versatile tool for the synthesis of a variety of block copolymers.[2] Among these methods, RAFT[3] and ATRP[4] have emerged as the most successful techniques due to their applicability to a wide range of monomers and mild reaction conditions. Although the CRP of many vinyl monomers is very effective, the preparation of well-defined block copolymers from both conjugated and non conjugated monomers remains challenging. Indeed, RAFT agents suitable for styrenic and (meth)acrylic monomers provide poor, or no control, over the polymerization of vinyl acetate (VAc) or *N*-vinylpyrrolidone (NVP) and *vice versa*. The problems associated with ATRP of VAc arise mainly from the difficult generation of propagating radicals from the dormant alkyl halide species.[5,6] The synthesis of well-defined ($M_w/M_n \leq 1.50$) poly(vinyl acetate) containing block copolymers by subsequent cobalt mediated radical polymerization of VAc and ATRP of styrene and (meth)acrylates was recently reported.[7] However this approach allows only for the preparation of block copolymers with an alkoxyamine function in their backbone which raises questions about the stability of these polymers at high temperature or over a long period of time. Consequently, we sought an alternative process for the synthesis of poly(vinyl acetate) containing block copolymers. Our approach employs the successive RAFT polymerization of VAc and ATRP of (meth)acrylates or styrenic monomers with a bromoxanthate iniferter and allows the preparation of well-defined ($1.15 \leq M_w/M_n \leq 1.24$) block copolymers.

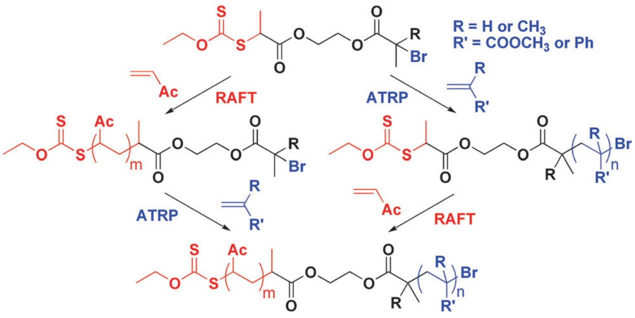
The bromoxanthate iniferters were prepared in three steps (Scheme 1). The esterification of 2-bromopropionyl bromide **2** with ethylene glycol **1** gave hydroxyethyl 2-bromopropionate **3** (77% yield). The xanthate moiety was subsequently introduced *via* nucleophilic substitution with potassium ethyl xanthogenate to form the hydroxyxanthate **4** (94% yield). The bromoxanthate iniferters **5** (79% yield) and **6** (99% yield) were obtained by condensation of **4** with 2-bromopropionyl and 2-bromoisobutyryl bromide, respectively.



Scheme 1 Synthesis of bromoxanthate iniferters. *Reagents and conditions:* (a) **1** (50 equiv.), pyridine (5 equiv.), THF 0 °C 1 h, 25 °C 16 h, 77%; (b) potassium ethyl xanthogenate (1.12 equiv.), acetone, 25 °C 12 h, 94%; (c) **2** (1.25 equiv.), pyridine (1.4 equiv.), CH_2Cl_2 0 °C 1 h, 25 °C 16 h, 79% or 2-bromoisobutyryl bromide (1.15 equiv.), pyridine (1.4 equiv.), CH_2Cl_2 0 °C 1 h, 25 °C 16 h, 99%.

Poly(vinyl acetate) containing block copolymers could be prepared by two different strategies using the bromoxanthate iniferters **5** and **6**. ATRP of (meth)acrylate or styrenic monomers could be conducted either before or after the RAFT polymerization of VAc (Scheme 2).

ATRP of methyl methacrylate (MMA), methyl acrylate (MA) and styrene (St) was conducted with **6** as an initiator. Polymers with low M_w/M_n and with good agreement between theoretical and experimental molecular weights were obtained for all three systems (Table 1). However, for MMA and St polymerizations, the size exclusion chromatography (SEC) traces were bimodal, which could indicate that polymerization took place to some extent through the xanthate moiety. The polymerization of MMA and St through the xanthate moiety could represent a problem for the subsequent polymerization of VAc, as it modifies the nature of the living group of the xanthate.



Scheme 2 Synthesis of poly(vinyl acetate) containing block copolymers by sequential ATRP and RAFT polymerization.

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Table 1 ATRP of MMA, MA and St with bromoxanthate iniferter **6**

M	M–**6**–Cu^0–CuBr–$CuBr_2$–L	Ligand	Conv. (%)	M_{nth}/g mol^{-1}	M_{nexp}/g mol^{-1})	M_w/M_n
MMA[a]	500 : 1 : 0 : 1 : 0.1 : 2.2	dNbpy	76.3	38 600	39 900	1.25
MA[b]	500 : 1 : 1 : 0 : 0 : 1	Me_6TREN	68.7	29 900	28 800	1.21
St[c]	150 : 1 : 1 : 0 : 0 : 1	PMDETA	49.7	7700	8800	1.35

[a] Conditions: MMA–anisole = 1 : 1 v/v, 90 °C, 10 h. [b] MA–acetone = 1 : 1 v/v, 25 °C, 3 h. [c] Bulk, 40 °C, 2 h 45.

Table 2 RAFT polymerization of VAc with PMMA, PMA and PS macroiniferters

Macroiniferter; M_n/g mol^{-1}; M_w/M_n	Time/h	Conv. (%)	M_{nth}/g mol^{-1}	M_{nexp}/ g mol^{-1}	M_w/M_n
PMMA; 7650; 1.26[a]	70	1.1	8600	8800	1.21
PMA; 5200; 1.36[b]	11	40.6	12 200	12 900	1.31
PS; 8050; 1.42[c]	47	2.3	8550	8350	1.50

[a] Conditions: [VAc] : [PMMA] : [AIBN] = 1000 : 1 : 1, bulk, 60 °C. [b] [VAc] : [PMA] : [AIBN] = 200 : 1 : 0.3, VAc–anisole = 2 : 1 v/v, 60 °C. [c] [VAc] : [PS] : [AIBN] = 200 : 1 : 0.3, VAc–anisole = 2 : 1 v/v, 60 °C.

The macroiniferters prepared by ATRP with **6** were subsequently used to mediate the RAFT polymerization of VAc (Table 2). A well-defined PMA-*b*-PVAc block copolymer with M_n = 12 900 (M_{nth} = 12 200) and M_w/M_n = 1.31 was obtained. However, in the case of PMMA and PS macroiniferters, essentially no polymerization took place. VAc lacks a conjugating substituent, and thus its propagating radical is highly reactive, less stable, and tends to undergo chain transfer reactions. The tertiary and secondary alkyl bromide chain ends in PMMA and PS macroiniferters, respectively, are likely to induce chain transfer to produce inactive Br–PVAc chain ends and radicals which are moderately reactive towards VAc.

Since conducting the ATRP of methyl methacrylate or styrene before the RAFT polymerization of VAc encounters the problems discussed above, VAc RAFT polymerization was carried out before the ATRP of (meth)acrylate or styrene monomers to suppress these side reactions. Thus, RAFT polymerization of VAc was conducted first with bromoxanthates **5** and **6** as chain transfer agents. When **6** was used as iniferter, only very low conversion could be reached (Table 3). The presence of a 2-bromoisobutyrate moiety within bromoxanthate **6** likely induces transfer with propagating VAc radicals, as discussed before. The resulting tertiary radicals react very slowly with VAc (k_i = 18 M^{-1} s^{-1} at 20 °C)[8] and predominantly terminate, reducing the polymerization rate and limiting monomer conversion.

On the other hand, the RAFT polymerization of VAc with **5** yielded poly(vinyl acetate) (PVAc) with M_n = 8350 (M_{nth} = 8550) and M_w/M_n = 1.29 (Table 3). The polymerization showed typical features of a controlled radical polymerization, *i.e.* constant concentration of propagating radicals with first order kinetics in monomer and a linear evolution of molecular weight with conversion. In addition, the value of M_w/M_n remained below 1.3 and SEC traces were monomodal (Fig. 1 and 2).

PVAc containing block copolymers were prepared by ATRP of St, MA and MMA with a PVAc macroiniferter (M_n = 2950; M_w/M_n = 1.26), **7**, prepared with **5** (Table 4). PVAc-*b*-PS, PVAc-*b*-PMA and PVAc-*b*-PMMA block copolymers with low M_w/M_n, ranging from 1.14 to 1.24, were obtained. In the case of St and MA polymerization, no unreacted macroiniferter could be detected in the SEC chromatograms (Fig. 3) and the initiation efficiencies were 88% and 87%, respectively. The inefficient chain transfer from vinyl acetate RAFT reagents, such as macroiniferter **7**, is anticipated based on computational results.[9] The transfer is endoenthalpic by 20.8 kJ mol^{-1} for MA and even more for St (33.6 kJ mol^{-1}). These values, assuming small entropy change in the transfer process, would correspond to very small values of equilibrium constant for transfer ($K \sim 2 \times 10^{-4}$ for MA and $K \sim 1 \times 10^{-6}$ for St). Experimental results are

Table 3 RAFT polymerization of VAc with bromoxanthate **5** and **6**

BX	VAc–BX–AIBN	Time/h	Conv. (%)	M_{nth}/g mol^{-1}	M_{nexp}/g mol^{-1}	M_w/M_n
5[a]	245 : 1 : 0.5	14	38.8	8550	8350	1.29
6[b]	200 : 1 : 0.2	50	4.7	1200	840	1.33

[a] Conditions: VAc–anisole = 4 : 1 v/v, 60 °C. [b] Bulk, 60 °C.

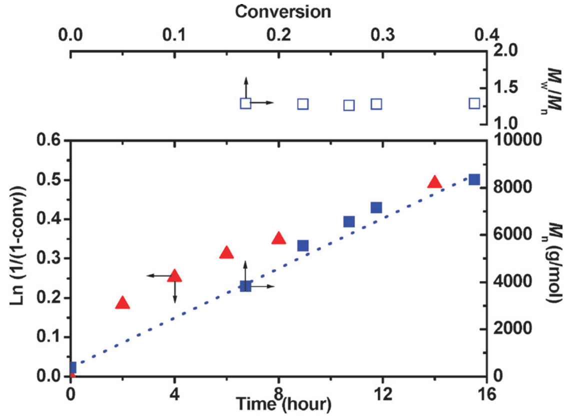

Fig. 1 Kinetics, M_n and M_w/M_n *vs.* conversion plots for VAc polymerization with **5**. [VAc] : [**5**] : [AIBN] = 245 : 1 : 0.5, VAc–anisole = 4 : 1 v/v, 60 °C.

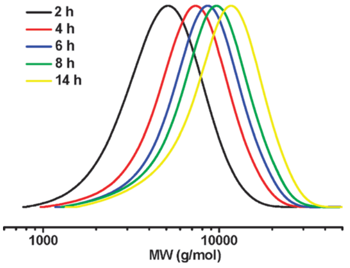

Fig. 2 Evolution of SEC traces during VAc polymerization with **5**. [VAc] : [**5**] : [AIBN] = 245 : 1 : 0.5, VAc–anisole = 4 : 1 v/v, 60 °C.

Table 4 ATRP of MMA, MA and St with PVAc macroiniferter **7**

M	M/**7**/Cu^0/CuBr/CuBr$_2$/L^a	Ligand	Conv. (%)	M_{nth}/g mol^{-1}	M_{nexp}/g mol^{-1}	M_w/M_n
St^b	525 : 1 : 0 : 0.9 : 0.1 : 1	PMDETA	44.2	27 100	30 700	1.20
MA^c	1200 : 1 : 1 : 0 : 0 : 1	Me$_6$TREN	64.2	69 300	79 600	1.14
MMA^d	560 : 1 : 0 : 1 : 0.1 : 2.2	bpy	66.4	40 600	57 500^e	1.32
MMA^f	560 : 1 : 0 : 1.8 : 0.2 : 4^g	bpy	76.2	46 100	54 900^h	1.24

[a] Conditions: **7**: M_n = 2950 g mol^{-1} and M_w/M_n = 1.26. [b] St–anisole = 1 : 1 v/v, 90 °C, 22 h. [c] MA–DMSO = 1 : 1 v/v, 25 °C, 20 min. [d] MMA–DMF = 1 : 1 v/v, 50 °C, 22 h. [e] After precipitation in methanol (before precipitation, M_n = 45 300 g mol^{-1} and M_w/M_n = 1.62). [f] MMA–DMF = 1 : 1 v/v, 50 °C, 24 h. [g] CuCl and CuCl$_2$ were used instead of CuBr and CuBr$_2$. [h] After precipitation in methanol (before precipitation, M_n = 50 500 g mol^{-1} and M_w/M_n = 1.34).

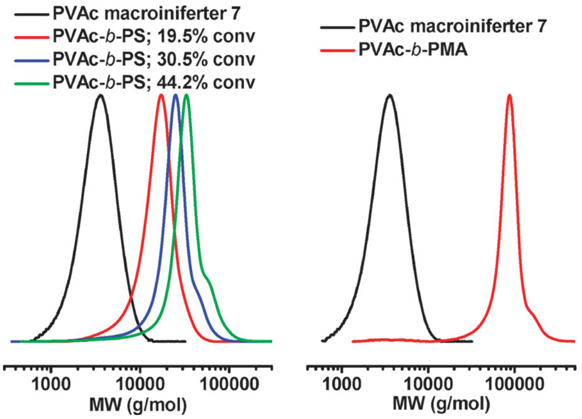

Fig. 3 Evolution of SEC traces during ATRP of St with PVAc macroiniferter **7** (left) and SEC trace of PVAc-*b*-PMA block copolymer prepared by ATRP of MA with PVAc macroiniferter **7** (right).

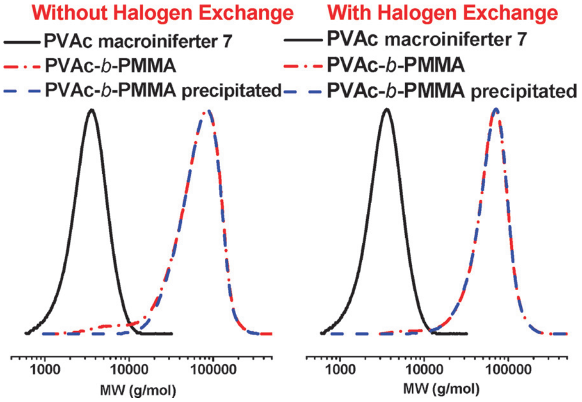

Fig. 4 SEC traces of PVAc-*b*-PMMA block copolymers (before and after precipitation in methanol) prepared by ATRP of MMA with a PVAc macroiniferter with (right) and without (left) halogen exchange.

in a very good agreement with theoretical predictions. When polymerizations of St, MA and MMA were initiated by AIBN in the presence of macroiniferter **7**, the unreacted macroiniferter remained in the reaction mixture and only uncontrolled high MW PS, PMA and PMMA were detected. This clearly shows the orthogonality of RAFT and ATRP for these systems.

When MMA was polymerized by ATRP with the macroiniferter **7**, an incomplete initiation (71% initiation efficiency) was obtained and some unreacted macroiniferter remained even at high conversion (Table 4, Fig. 4). The unreacted PVAc macroiniferter was easily removed by precipitation of the block copolymer in methanol to yield pure PVAc-*b*-PMMA block copolymer (Table 4, Fig. 4). The limited initiation efficiency in ATRP of methacrylate monomers from acrylate or styrene-based (macro)initiators, like **7**, is due to a greater apparent rate constant of propagation than that of cross-propagation. A procedure known as "halogen exchange" was developed to overcome poor initiation efficiency for such systems.[10] In this technique, the bromine end-group of the initiator is exchanged with a less labile chlorine for the dormant chain which decreases the apparent rate constant of propagation. "Halogen exchange" was thus used to prepare PVAc-*b*-PMMA block copolymers from the macroiniferter **7**. The initiation efficiency was significantly improved (84%) and only a small amount of unreacted PVAc was observed on SEC traces (Fig. 4). After precipitation in methanol, pure PVAc-*b*-PMMA block copolymer was obtained with a M_w/M_n as low as 1.24 (Table 4, Fig. 4).

A bromoxanthate iniferter was synthesized in three high yield steps and successfully used to selectively conduct the RAFT polymerization of VAc through the xanthate moiety. The PVAc macroiniferter was subsequently used to prepare well-defined PVAc-*b*-PS, PVAc-*b*-PMA and PVAc-*b*-PMMA block copolymers (1.15 ≤ M_w/M_n ≤ 1.24) by ATRP of styrene and methyl (meth)acrylate, providing the first example of a dual initiator for the ATRP and RAFT polymerization of conjugated and non conjugated monomers.[11,12] This approach offers a very efficient, straightforward and universal method to prepare poly(vinyl acetate) containing block copolymers.

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