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Polystyrene-*block*-poly(vinyl acetate) through the Use of a Switchable RAFT Agent

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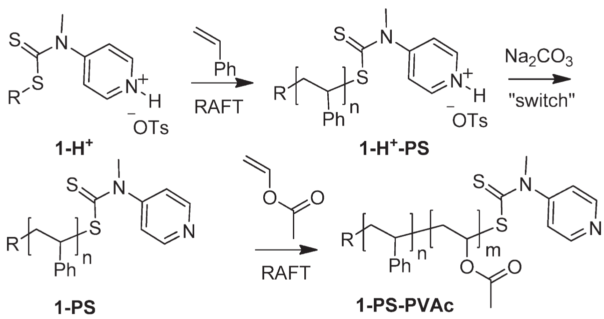
Radical polymerization with reversible addition−fragmentation chain transfer (RAFT polymerization) is a reversible deactivation radical polymerization and one of the most versatile processes for conferring living characteristics on radical polymerization.[1,2] The polymerization of most monomers polymerizable by radical polymerization can be controlled by the RAFT process. However, the RAFT agent ($ZC(=S)S-R$) needs to be selected according to the monomer(s) used. RAFT agents such as dithioesters (Z = aryl or alkyl) or trithiocarbonates (Z = alkylthio) suitable for controlling polymerization of the "more activated" monomers (MAMs) (e.g., MA, S)[3] inhibit or retard polymerizations of the "less activated" monomers (LAMs) (e.g., VAc, NVP). Similarly, RAFT agents suitable for controlling polymerizations of LAMs such as *N*,*N*-dialkyl- or *N*-alkyl-*N*-aryl dithiocarbamates and xanthates tend to be ineffective with MAMs. A consequence is that the synthesis of narrow polydispersity polyMAM-*block*-polyLAM is difficult or not possible using the conventional RAFT process.

Several groups[4−9] have reported strategies to overcome this barrier. These include processes where a first block comprising the MAM is prepared by atom transfer radical polymerization (ATRP), the ATRP initiator functionality (a bromine end group) is converted to a xanthate end group, and the resultant macro-RAFT agent is then used in the synthesis of a polyMAM-*block*-polyLAM.[4,5] including PS-*block*-PNVP.[5] Compounds that combine RAFT agent and ATRP initiator functionality in the one molecule[6,7] have also been used to synthesize polyMAM-*block*-polyLAM, including PS-*block*-PVAc.[7] There are reports of direct synthesis of polyMAM-*block*-polyLAM using other mechanisms.[8,9] Stibine-mediated polymerization was used to synthesize PS-*block*-PNVP.[8] Click chemistry (copper-catalyzed 1,3-dipolar addition) has been used to link RAFT-synthesized polyLAM and polyMAM blocks.[9]

We recently reported on a new class of stimuli-responsive RAFT agents that can be "switched" to offer good control over polymerization of both MAMs and LAMs and thus a more convenient route to polyMAM-*block*-polyLAM with narrowed molecular weight distributions.[10] This approach was demonstrated with the use of 4-pyridinyl-*N*-methyldithiocarbamate derivatives to prepare PMMA-*block*-PVAc and PMA-*block*-PNVC. The *N*-4-pyridinyl-*N*-methyldithiocarbamates provide effective control over polymerization of LAMs and when protonated also provide excellent control over the polymerization of MAMs.[10]

In applying the method to polyMAM-*block*-polyLAM, it was found that the block comprising MAMs needed to be synthesized first. This sequence is necessary because polyLAM$^\bullet$ are poor radical leaving groups with respect to polyMAM$^\bullet$, and consequently, polyLAM macro-RAFT agents can have very low transfer constants in MAM polymerization.

Scheme 1. Synthesis of Polystyrene-*block*-poly(vinyl acetate) (R = $CH(CH_3)CO_2CH_3$)



Attempts to synthesize PS-*block*-PVAc or other PS-*block*-polyLAM starting from a PS macro-RAFT agent prepared with a 4-pyridinyl-*N*-methyldithiocarbamate using the RAFT polymerization conditions (initiator:RAFT agent ∼ 1:10) that had proved successful for other polyMAM-*block*-polyLAM or PS-*block*-polyMAM gave no significant yield of polymer for an extended period ($>$4 h). This is attributed to the very low rate of PS$^\bullet$ addition to VAc, possibly compounded by the presence of trace amounts of styrene monomer in the PS macro-RAFT agent.[11] Styrene is well-known to inhibit the polymerization of VAc, which is a consequence of adverse reactivity ratios (r_S = 22.3, r_{VAc} = 0.02).[12] The rate constants for benzyl radical (a simple model for PS$^\bullet$) addition to styrene and VAc are 1100 and 15 M s^{-1}, respectively (25 °C).[13] These and other issues are discussed in recent papers on the selection of "R" to provide efficient initialization in polymerization of NVP and VAc.[14]

Several approaches to overcoming this dilemma have been investigated. One strategy is to use a larger than usual ratio of initiator to RAFT agent (e.g., 1:2 rather than the recommended 1:10).[2] The premise is that once the macro-RAFT agent has been converted to a new macro-RAFT agent with VAc as the terminal monomer unit polymerization should proceed normally. In the first step (Scheme 1), the protonated RAFT agent **1-H$^+$** was used to control the polymerization of styrene to form **1-H$^+$-PS**. This macro-RAFT agent was then neutralized, forming **1-PS**, and used in VAc polymerization to provide the desired **1-PS-PVAc**. Results are provided in Table 1 (experiments 1−7) and Figure 1a. A short period ($<$2 h) of retarded polymerization was observed, while the **1-PS** was converted to **1-PS-PVAc**, after which rapid polymerization was observed. However, the formation of some dead polystyrene by combination of PS$^\bullet$ radicals from **1-PS** is clearly evident in the UV262[15] distribution but not in the UV290 distribution (Figure 1a) and is less evident in the refractive index (RI) distribution (dominated by PVAc for high conversion samples) after the first time point. The presence of dead polystyrene accounts for the high Đ (molecular weight dispersity[16]) of **1-PS-PVAc** prepared with a high initiator concentration (Table 1). The living polymer which is seen in UV290 distribution (Figure 1a) has a relatively narrow molecular weight distribution.

Other strategies follow from the observation that it is possible to synthesize low Đ PS-*block*-PMA and PMA-*block*-PVAc.[10] Thus, **1-PS-MA-VAc** was successfully prepared as shown in Scheme 2 in three steps with isolation of **1-PS-MA** (Table 1,

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Table 1. Details of Polymer Syntheses

expt	RAFT agent[a]	$10^{-2}M$[b]	monomer[c]	M[b]	temp/°C	solvent	initiator[c]	$10^{-2}M$[b]	$M_n/10^3$ [d,f]	Đ[e,f]	time/h	conv/%
1	**1-H**$^+$[g]	7.0	S	8.75	90	bulk	ACHN	1.01	1.8 (1.9)	1.22(1.11)	2.0	18
2	**1-PS**	1.08	VAc	10.86	70	bulk	AIBN	0.57	5.4 (7.9)	2.16(1.81)	2.0	4.6
3	**1-PS**	1.08	VAc	10.86	70	bulk	AIBN	0.57	10.4 (13.3)	1.91(1.62)	2.5	13
4	**1-PS**	1.08	VAc	10.86	70	bulk	AIBN	0.57	18.2 (27.0)	2.00(1.42)	3.0	23
5	**1-PS**	1.08	VAc	10.86	70	bulk	AIBN	0.57	27.7 (39.9)	1.90(1.40)	3.5	37
6	**1-PS**	1.08	VAc	10.86	70	bulk	AIBN	0.57	50.2 (59.5)	1.83(1.61)	4.0	67
7	**1-PS**	1.08	VAc	10.86	70	bulk	AIBN	0.11	52.4	1.37	16.0	55
8	**1-H**$^+$[g]	7.0	S	8.75	90	bulk	ACHN	1.01	1.8	1.33	2.0	20
9	**1-PS-H**$^+$[g]	1.06	MA	5.52	70	benzene	AIBN	1.0	21.5	1.15	2.0	25
10	**1-PS-PMA**	0.046	VAc	10.86	70	bulk	AIBN	0.50	52.0	1.48	15.0	75
11	**1-PS**	1.08	VAc/MA	10.3/0.55	70	bulk	AIBN	0.11	6.6	2.90	2.0	6.6
12	**1-PS**	1.08	VAc/MA	10.3/0.55	70	bulk	AIBN	0.11	14.1	2.04	4.0	13
13	**1-PS**	1.08	VAc/MA	10.3/0.55	70	bulk	AIBN	0.11	25.1	1.58	6.0	25
14	**1-PS**	1.08	VAc/MA	10.3/0.55	70	bulk	AIBN	0.11	42.7	1.31	8.0	36

[a] The macro-RAFT agent formed in experiment 1 was neutralized and used in experiments 2−7 and 11−14. That formed in experiment 8 was used in experiment 9. That formed in experiment 9 was neutralized and used in experiment 10. [b] Concentrations at 22 °C. [c] Abbreviations: MA = methyl acrylate, S = styrene, VAc = vinyl acetate, AIBN = azobis(isobutyronitrile), ACHN = azobis(1-cyclohexanenitrile). [d] Number-average molecular weight in polystyrene equivalents for conventional analysis of RI trace (see Figure 1). [e] Dispersity (Đ) = M_w/M_n = ratio of weight-average to number-average molecular weight. [f] M_n and Đ for **1-PS-PVAc** from analysis of UV 290 trace is given in parentheses (excludes contribution from dead polymer). [g] Acid used was *p*-toluenesulfonic acid.

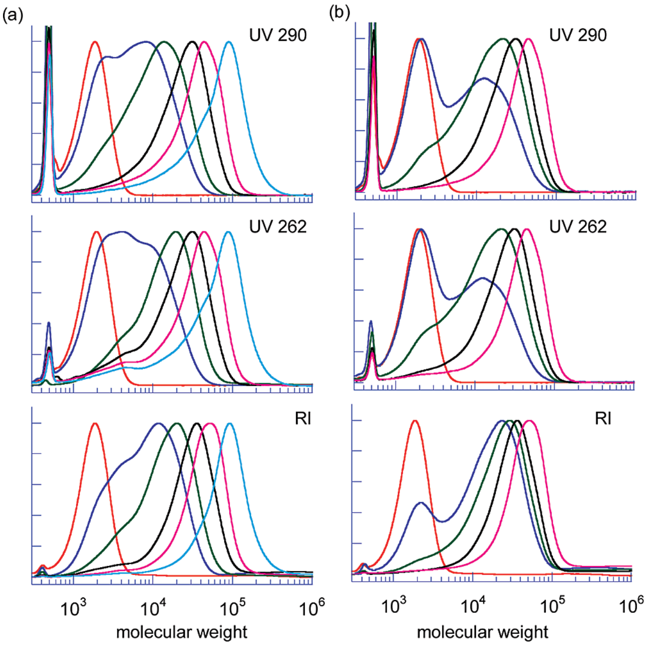
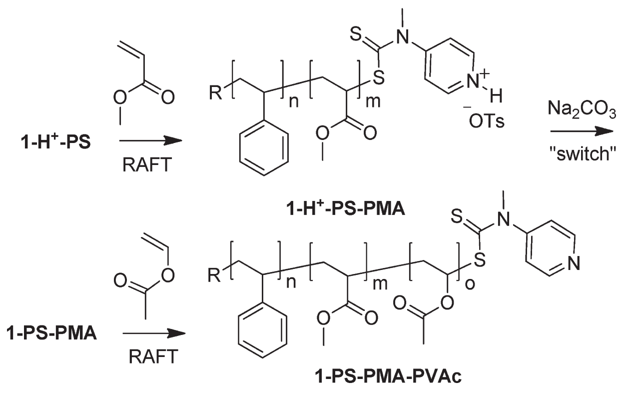


Figure 1. Evolution of normalized molecular weight distributions with conversion for (a) polystyrene-*block*-poly(vinyl acetate) obtained at 0, 2, 2.5, 3, 3.5, and 4 h (left to right) and (b) polystyrene-*block*-poly(methyl acrylate-*grad*-vinyl acetate)-*block*-poly(vinyl acetate) obtained at 0, 2, 4, 6, and 8 h (left to right) from gel permeation chromatograms with (RI) with refractive index detector, (UV 262) with UV detector at 262 nm, and (UV 290) at 290 nm.[15] For polymerization conditions see Table 1.

experiments 8−10). A more convenient process is to copolymerize a mixture of MA and VAc in the presence of the PS macro-RAFT agent (**1-PS**) in its deprotonated form. The deprotonated **1-PS** has only a low transfer constant in MA polymerization[10] and is consumed slowly. However, the higher reactivity of MA toward both PS$^\bullet$ and PVAc$^\bullet$[17] dictates that PS-*block*-P(MA-*grad*-VAc)-*block*-PVAc[2,18] should be formed and that polymerization proceeds with no discernible inhibition period (Table 1, experiments 11−14) and without significant formation of dead polystyrene (as shown by close correspondence of UV 262 and UV 290 traces in Figure 1b). In the copolymerization experiment the MA:VAc ratio was 1:20, and the NMR analysis is consistent with the MA, and the initial macro-RAFT agent, being largely consumed before a total monomer conversion of 25%.

Scheme 2. Synthesis of Polystyrene-*block*-poly(methyl acrylate)-*block*-poly(vinyl acetate) (R = $CH(CH_3)CO_2CH_3$)



This paper reports the application of "switchable" RAFT agents to the synthesis of PS-*block*-poly(VAc) (a) directly, (b) as PS-*block*-poly(MA)-*block*-poly(VAc), and (c) as PS-*block*-poly(MA-*grad*-VAc)-*block*-poly(VAc). Process (a) is complicated by an inhibition period and the formation of some dead polymer, (b) is a three-step process but should generally yield a product of higher purity, and (c) is most convenient but, because of the slow rate of consumption of the macro-RAFT agent, is only suitable when a longer PVAc block is required. Variations on these procedures involving the use of monomers other than MA and other polymerization conditions are currently being explored.

Supporting Information Available: Experimental procedures for RAFT polymerizations and polymer characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Publication. This communication posted ASAP on November 16, 2009. The last reference in reference 1 has been revised. The correct version posted on November 19, 2009.

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(3) Abbreviations: LAM = less activated monomer, MA = methyl acrylate, MAM = more activated monomer, NVP = *N*-vinylpyrrolidone, S = styrene, VAc = vinyl acetate, PMA = poly(methyl acrylate), PMMA = poly(methyl methacrylate), PNVP = poly(*N*-vinylpyrrolidone), PS = polystyrene, PVAc = poly(vinyl acetate), and RAFT = reversible addition−fragmentation chain transfer, PNVC = poly(*N*-vinyl carbazole).

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