

Supporting Information

Synthesis of Micrometer-sized Poly(vinyl acetate) Particles through Microsuspension Iodine Transfer Polymerization: Effect of Iodine Species in a Water Medium

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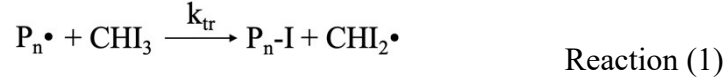
Number of pages: 14
Number of figures: 7
Number of schemes: 2
Number of Tables: 8

Contents:

1. Calculation of chain transfer constant (C_{tr}) at different temperatures
2. Simulation section
3. Calculation of maximum monomer units of an oligomer radical (P_{max})
4. Appearance of PVAc synthesized at 60 °C before and after dissolving in DMF
5. Evolution molecular weight (M_n) and molecular weight distribution (M_w/M_n) of PVAc
6. Livingness of PVAc prepared by *ms* ITP
7. Scheme of ITP in bulk system with iodoform as chain-transfer agent
8. Evolution appearance of PVAc dispersions prepared by *ms* ITP using V-70 as initiator at 30 °C
9. UV-vis absorption spectra
10. Colloid stability of PVAc prepared by *ms* ITP and *ms* CRP
11. Alcoholysis of PVAc
12. Chain transfer to PVAc in *ms* CRP and *ms* CRP of VAc
13. Reference

Calculation of chain transfer constant (C_{tr}) at different temperatures¹

The main chain transfer appeared in the early stage of the polymerization showed as below:



This reaction is a second-order reaction, therefore, the consumption of iodoform (CHI_3) within the period of time (t) based on reaction (1) can be calculated by equation (1) through the following mathematical procedures.

$$\begin{aligned} \text{Consumption of } [CHI_3] - \frac{d[CHI_3]}{dt} &= \bar{k}_{tr} [P_n \bullet][CHI_3] \implies - \frac{d[CHI_3]}{[CHI_3]} = \bar{k}_{tr} [P_n \bullet] dt \\ \downarrow \text{Integration} & \\ - \int_{[CHI_3]_0}^{[CHI_3]_t} \frac{d[CHI_3]}{[CHI_3]} &= \int_0^t \bar{k}_{tr} [P_n \bullet] dt \implies \ln \left(\frac{[CHI_3]_0}{[CHI_3]_t} \right) = \bar{k}_{tr} [P_n \bullet] t \quad \text{eq (1)} \end{aligned}$$

In the calculation, the k_{tr} , $[CHI_3]_0$, $[CHI_3]_t$ and $[P_n \bullet]$ refer to the chain transfer rate, concentration of CHI_3 at time $t = 0$ and $t = t$, and concentration of polymer radicals, respectively.

For the generally propagation:



The generation of polymer within the period of time (t) based on reaction (2) can be calculated by equation (2) through the following mathematical procedures.

$$\begin{aligned} \text{Consumption of } [M] - \frac{d[M]}{dt} &= \bar{k}_p [P_n \bullet][M] \implies - \frac{d[M]}{[M]} = \bar{k}_p [P_n \bullet] dt \\ \downarrow \text{Integration} & \\ - \int_{[M]_0}^{[M]_t} \frac{d[M]}{[M]} &= \int_0^t \bar{k}_p [P_n \bullet] [M] dt \implies \ln \left(\frac{[M]_0}{[M]_t} \right) = \bar{k}_p [P_n \bullet] t \quad \text{eq (2)} \end{aligned}$$

The k_p , $[M]$, $[CHI_3]_t$ and $[P_n \bullet]$ refer to the propagation rate, the concentration of monomer, the concentration of CHI_3 at time t , and the concentration of polymer radicals, respectively.

After dividing eq (1) by eq (2), it gives the below equation (3):

$$\ln \left(\frac{[CHI_3]_0}{[CHI_3]_t} \right) = \frac{\bar{k}_{tr}}{\bar{k}_p} \ln \left(\frac{[M]_0}{[M]_t} \right) \quad \text{eq (3)}$$

Because $C_{tr} = k_{tr}/k_p$, eq (3) can be converted into the following equation (4), which can be used to calculate C_{tr} experimentally in the form of conversion.

$$C_{tr} = \ln(1 - p) / \ln(1 - q) \quad \text{eq (4)}$$

In equation (4), the p and q represent the conversion of CHI_3 and monomer, respectively, which can be determined by GC. The measurement was proceeded in the bulk system with the same concentration of materials as the recipe in the suspension system. As a small amount of I_2 generated in the early stage, which can work as the good scavenger for radicals and result in the inhibition of polymerization, the value of C_{tr} was focused within the early 15 minutes.

The values of C_{tr} at different temperatures in the existence of different initiators was given in Table S1.

Table S1. Calculated Values of C_{tr} of CHI_3 at different temperatures with different initiators.

Monomer	T (°C)	Initiator	C_{tr}
MA	70	BPO	50.62
	60	AIBN	5.43
VAc	50	V-70	2.28
	40	V-70	21.54
	30	V-70	40.16

Simulation section²

For simplifying the simulation, the polymerization rate in the aqueous phase (R_p^w) only takes the saturation solubilities of monomers, initiators, and iodoform in water into account.

The kinetic scheme for simulation is given in Table S2. And the kinetic parameters input to the simulation model are given in Table S3.

Table S2. Kinetic scheme for simulation of ITP.

<i>Primary radical formation</i>		<i>Chain transfer</i>	
$I \rightarrow f \times (R\bullet + R\bullet)$	k_d	$P1(s)\bullet + P2-I(r) \rightarrow P1-I(s) + P2(r)\bullet$	k_{ex}
<i>Initiation</i>		$P1(s)\bullet + P3-I(r) \rightarrow P1-I(s) + P3(r)\bullet$	k_{ex}
$R\bullet + M \rightarrow P1(1)\bullet$	$k_{i,R\bullet}$	$P2(s)\bullet + P1-I(r) \rightarrow P2-I(s) + P1(r)\bullet$	k_{ex}
$CHI_2\bullet + M \rightarrow P2(1)\bullet$	$k_{i,CHI_2\bullet}$	$P2(s)\bullet + P2-I(r) \rightarrow P2-I(s) + P2(r)\bullet$	k_{ex}
$R\bullet + M \rightarrow P3(1)\bullet + RH$	k_{itrM}	$P2(s)\bullet + P3-I(r) \rightarrow P2-I(s) + P3(r)\bullet$	k_{ex}
<i>Propagation</i>		$P3(s)\bullet + P1-I(r) \rightarrow P3-I(s) + P1(r)\bullet$	k_{ex}
$P1(s)\bullet + M \rightarrow P1(s+1)\bullet$	k_p	$P3(s)\bullet + P2-I(r) \rightarrow P3-I(s) + P2(r)\bullet$	k_{ex}
$P2(s)\bullet + M \rightarrow P2(s+1)\bullet$	k_p	$P3(s)\bullet + P3-I(r) \rightarrow P3-I(s) + P3(r)\bullet$	k_{ex}
$P3(s)\bullet + M \rightarrow P3(s+1)\bullet$	k_p	<i>Termination</i>	
<i>Chain transfer</i>		$P1(s)\bullet + P1(r)\bullet \rightarrow D11(s+r)$	k_{tc}
$R\bullet + CHI_3 \rightarrow RI + CHI_2\bullet$	k_{itr,CHI_3}	$P2(s)\bullet + P2(r)\bullet \rightarrow D22(s+r)$	k_{tc}
$P1(s)\bullet + RI \rightarrow P1-I(s) + R\bullet$	$k_{tr,RI}$	$P3(s)\bullet + P3(r)\bullet \rightarrow D33(s+r)$	k_{tc}
$P2(s)\bullet + RI \rightarrow P2-I(s) + R\bullet$	$k_{tr,RI}$	$P1(s)\bullet + P2(r)\bullet \rightarrow D12(s+r)$	k_{tc}
$P3(s)\bullet + RI \rightarrow P3-I(s) + R\bullet$	$k_{tr,RI}$	$P1(s)\bullet + P3(r)\bullet \rightarrow D13(s+r)$	k_{tc}
$P1(s)\bullet + M \rightarrow D1(s) + P3(1)\bullet$	k_{trm}	$P2(s)\bullet + P3(r)\bullet \rightarrow D23(s+r)$	k_{tc}
$P2(s)\bullet + M \rightarrow D2(s) + P3(1)\bullet$	k_{trm}	$P1(s)\bullet + P1(r)\bullet \rightarrow D1(s) + D1(r)$	k_{td}
$P3(s)\bullet + M \rightarrow D3(s) + P3(1)\bullet$	k_{trm}	$P2(s)\bullet + P2(r)\bullet \rightarrow D2(s) + D3(r)$	k_{td}
$P1(s)\bullet + CHI_3 \rightarrow P1-I(s) + CHI_2\bullet$	k_{tr,CHI_3}	$P3(s)\bullet + P3(r)\bullet \rightarrow D3(s) + D3(r)$	k_{td}
$P2(s)\bullet + CHI_3 \rightarrow P2-I(s) + CHI_2\bullet$	k_{tr,CHI_3}	$P1(s)\bullet + P2(r)\bullet \rightarrow D1(s) + D2(r)$	k_{td}
$P3(s)\bullet + CHI_3 \rightarrow P3-I(s) + CHI_2\bullet$	k_{tr,CHI_3}	$P1(s)\bullet + P3(r)\bullet \rightarrow D1(s) + D3(r)$	k_{td}
$P1(s)\bullet + P1-I(r) \rightarrow P1-I(s) + P1(r)\bullet$	k_{ex}	$P2(s)\bullet + P3(r)\bullet \rightarrow D2(s) + D3(r)$	k_{td}

Table S3. Kinetic input parameters for simulation and recipes of ITP of VAc or MA.

<i>Coefficient</i>	<i>eq for VAc</i>	<i>eq for MA</i>
<i>k d</i> (s ⁻¹)	= 5.37 × 10 ¹¹ exp(-94300/RT) ^{a)} for V-70 = 5.82 × 10 ¹⁵ exp(-132400/RT) ^{a)} for AIBN R=8.314J K ⁻¹ mol ⁻¹	= 3 × 10 ¹³ exp(-123800/RT) ^{a)} for BPO R=8.314J K ⁻¹ mol ⁻¹
<i>k i,R•</i> (M ⁻¹ s ⁻¹)	= <i>k_p</i>	= <i>k_p</i>
<i>k i,CHI₂•</i> (M ⁻¹ s ⁻¹)	= <i>k_p</i>	= <i>k_p</i>
<i>k itr_m</i> (M ⁻¹ s ⁻¹)	= <i>k_p</i> /100	= <i>k_p</i> /100
<i>k p</i> (M ⁻¹ s ⁻¹)	= 2.43 × 10 ⁸ exp(-30600/RT) ^{b)} R=8.314J K ⁻¹ mol ⁻¹	= 1.66 × 10 ⁷ exp(-17700/RT) ^{c)} R=8.314J K ⁻¹ mol ⁻¹
<i>k itr,CHI₃</i> (M ⁻¹ s ⁻¹)	= <i>k_{tr,CHI₃}</i>	= <i>k_{tr,CHI₃}</i>
<i>k tr,RI</i> (M ⁻¹ s ⁻¹)	= <i>k_{tr,CHI₃}</i>	= <i>k_{tr,CHI₃}</i>
<i>k tr_m</i> (M ⁻¹ s ⁻¹)	= 1.9 × 10 ⁻⁴ × <i>k_p</i> ^{d)}	= 0.224 × 10 ⁻⁴ × <i>k_p</i> ^{d)}
<i>k tr,CHI₃</i> (M ⁻¹ s ⁻¹)	= C _{tr} × <i>k_p</i> ^{e)}	= C _{tr} × <i>k_p</i> ^{e)}
<i>k ex</i> (M ⁻¹ s ⁻¹)	= <i>k tr,CHI₃</i>	= <i>k tr,CHI₃</i>
<i>k t</i> (M ⁻¹ s ⁻¹)	= 2.08 × 10 ¹¹ exp(-5204/RT) ^{f)} R=1.987cal K ⁻¹ mol ⁻¹	= 1.40 × 10 ¹⁰ exp(-5300/RT) ^{g)} R=1.987cal K ⁻¹ mol ⁻¹
[M] _{aq} (mol/L) ^{h)}	3.19 × 10 ⁻¹	6.72 × 10 ⁻¹
[I] _{aq} (mol/L) ⁱ⁾	6.5 × 10 ⁻³ for AIBN 3.70 × 10 ⁻⁴ for V-70	4.6 × 10 ⁻⁴ for BPO
[CHI ₃] _{aq} (mol/L) ^{j)}	2.54 × 10 ⁻⁴	2.54 × 10 ⁻⁴

a) <https://specchem-wako-jp.fujifilm.com/en/oilazo>

b) M. S. Matheson, E. E. Auer, Ellen B. Bevilacqua, *et al.*, *J. Am. Chem. Soc.*, **1949**, *71*, 2610

c) X. Yu, J. Pfaendtner, and L. J. Broadbelt, *J. Phys. Chem. A.*, **2008**, *112*, 6772

d) Brandrup, J.; Immergut, E. H.; Grulke, E.A., *Polymer Handbook, Fourth Edition*. **1998**, II-99,101

e) C_{tr} shown in Table S1

f) Matheson, S.; Auer, E. E.; Bevilacqua, Ellen B.; Hart, E. J., *J. Am. Chem. Soc.* **1949**, *71*, 2610

g) Matheson, S.; Auer, E. E.; Bevilacqua, Ellen B.; Hart, E. J., *J. Am. Chem. Soc.* **1949**, *71*, 497

h) D. Richon, and A. Viillard, *Fluid Ph. Equilibria.*, **1985**, *21*, 279

i) Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02

j) Kamal I. Al-Malah, *J. Mol. Model.*, **2011**, *17*, 1029

Calculation of maximum monomer units of an oligomer radical (P_{\max})

The hydrophobic free energy (ΔG^{hyd}) can be seen as the important factor to influence the ratios of the adsorption to desorption rate coefficients.³ If the oligomers in water phase possess the larger ΔG^{hyd} , the oligomers have higher possibility of “instantaneous” entry to the monomer droplets, that is, they are less likely to desorb after entering and proceed to propagation in the monomer droplet.

The ΔG^{hyd} of small solute molecules in water was calculated by the eq (5), which proposed by Israelachvili and Pashley.⁴ Here σ is the diameter of the solute molecule. In the case of polymerization with water-insoluble initiator BPO, the σ of a styryl unit, a methene group and a carbon monoxide are 0.6 nm,⁵ 0.15 nm⁶ and 0.13 nm,⁷ respectively. While, in the case of AIBN and V-70, only the lengths of C-H (0.109 nm) and C-C bond (0.15 nm) are taken into consideration.

$$\Delta G_1^{\text{hyd}} \text{ (kJ/mol)} \cong -20 \sigma \quad \text{eq (5)}$$

The ΔG^{hyd} of monomer in water was calculated by the eq (6),³ where the $[M_{\text{aq,sat}}]$ refers to the saturation solubility of the monomer in the aqueous phase (mol L⁻¹), gas constant (R) is 1.987 cal K⁻¹mol⁻¹ and T is thermodynamic temperature.

$$\Delta G_2^{\text{hyd}} \text{ (kJ/mol)} \cong 0.004RT \ln[M_{\text{aq, sat}}] \quad \text{eq (6)}$$

In the calculation, a criterion was set up that the ΔG^{hyd} for oligomers is approximate to the sum of the ΔG^{hyd} of monomer units. Before the oligomers become incipiently insoluble in water, there is a maximum monomer units of oligomer radicals (P_{\max}) which can still exit from monomer droplets. This maximum value can be estimated roughly by considering the n-alkyl chain length, that the ΔG^{hyd} of both oligomer and n-alkyl specie is equal. In the case of emulsifier-free emulsion polymerization using BPO as initiator, the ΔG^{hyd} of n-alkyl benzoate is required. For n-alkyl benzoate in the aqueous phase, which is found “absolutely” insoluble in water when the number of methene groups is 4. It is determined by comparing with the water solubility of heptadecyl sulfate, which is found experimentlly that oligomeric species becomes insoluble in water.^{6, 8, 9} For using AIBN and V-70 as initiator, the “absolutely” insoluble species appear when the number of methene groups are 16 and 14, respectively, after comparing the predicted water solubility to the heptadecyl sulfate.

When $|\Delta G_2^{\text{hyd}}|$ of initial radicals is higher than the $|\Delta G_1^{\text{hyd}}|$ calculated by eq (5), the insoluble oligomer radicals will start to appear.

Therefore, the value of the P_{\max} can be obtained by eq (7). Here the integer function (int) rounds off the quantity to the lower integer value.

$$P_{\max} = \text{int}(\Delta G_1^{\text{hyd}} / \{0.004RT \ln[M_{\text{aq, sat}}]\}) \quad \text{eq (7)}$$

The exact maximum units of oligomer which can still exit to water phase at different temperatures were shown in Table S4.

Table S4. Calculated Values of P_{\max} for MA and VAc at various temperature using different initiators.

Monomer	T (°C)	Initiator	$[M_{\text{aq, sat}}]$ (mol/L)	ΔG_1^{hyd} (KJ/mol)	P_{\max}
MA	70	BPO	0.697	-26.6	26
	60	AIBN			16
VAc	50	V-70	0.290	-55.4	17
	40	V-70			17
	30	V-70			18

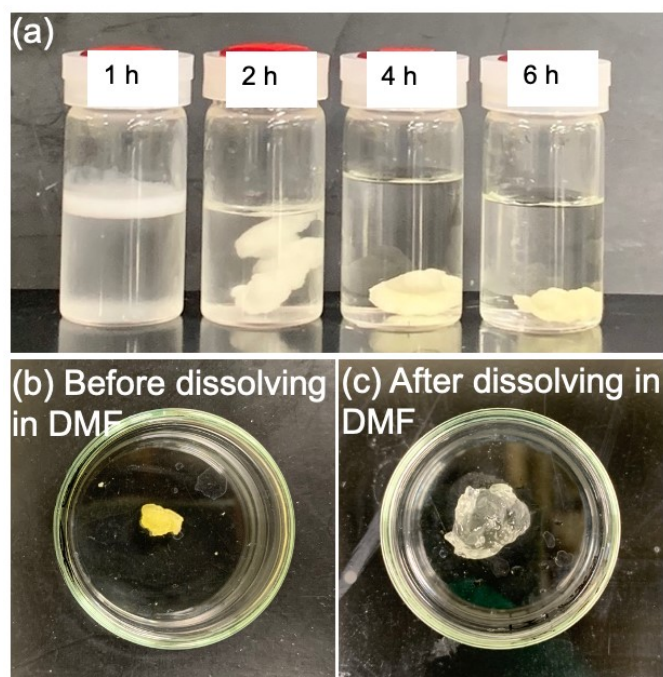


Figure S1. Time-dependent appearance of PVAc dispersions prepared by *ms* ITP using AIBN as initiator at 60 °C (a), and the appearance of PVAc coagulation before (b) and after (c) dissolving in DMF for 24 h.

Table S5. Evolution molecular weight, theoretical molecular weight, and molecular weight distribution of PVAc.

	Time (h)	Conversion (%)	M_n (g/mol)	$M_{n,th}$ (g/mol)	M_w/M_n
<i>ms</i> ITP	4	14.9	3,700	4,900	1.19
	8	16.5	6,300	5,400	1.36
	10	31.1	9,400	10,000	1.55
	12	42.9	13,600	14,000	1.68
	15	45.8	17,400	15,000	1.73
	18	79.4	24,000	25,900	1.95
	24	82.2	26,000	26,900	2.00
<i>ms</i> CRP	6	48.4	122,600	—	5.08

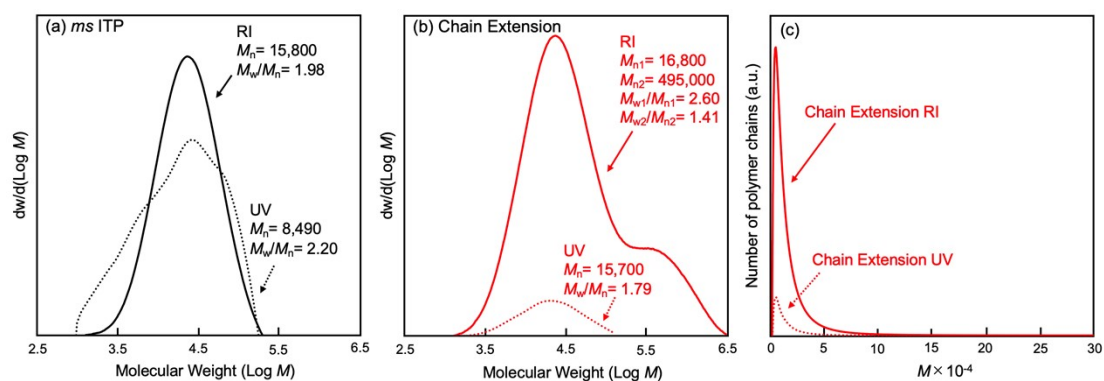
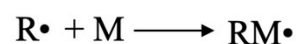
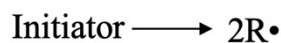
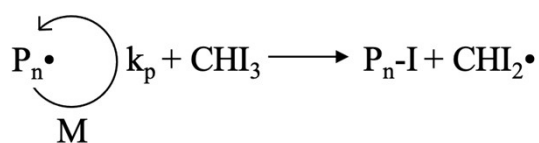


Figure S2. Molecular weight distributions of PVAc prepared by *ms* ITP (a) and the obtained Polymer after chain extension ITP in dispersion (b), and number distributions of the obtained polymer after chain extension ITP in dispersion (c). (RI, solid line; UV, dash line).

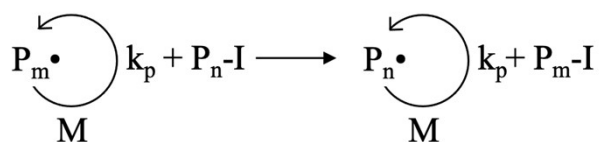
Initiation



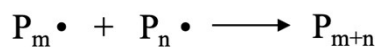
Chain
Transfer



Degenerative
transfer



Termination



Scheme S1. General Reaction of Iodine Transfer Polymerization (ITP) with iodoform as chain-transfer agent.

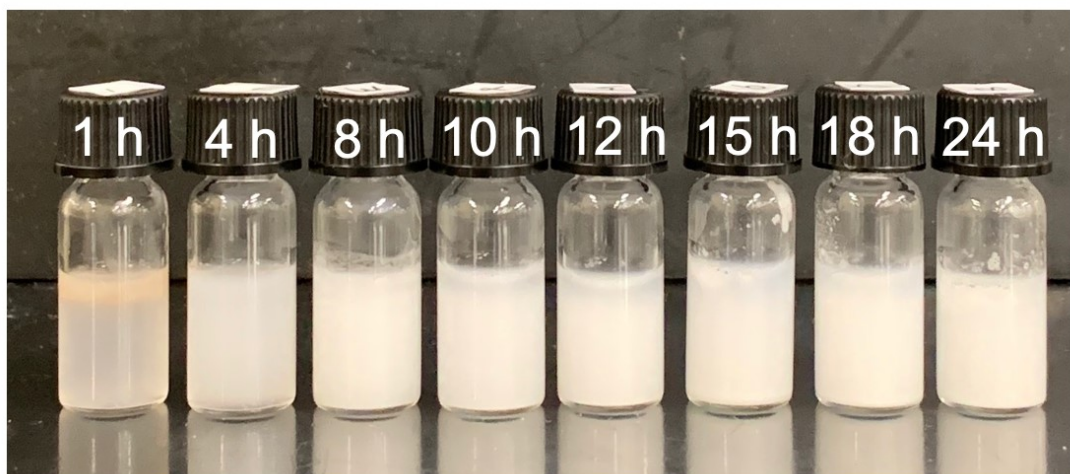


Figure S3. Evolution appearance of PVAc dispersions prepared by *ms* ITP using V-70 as initiator at 30 °C

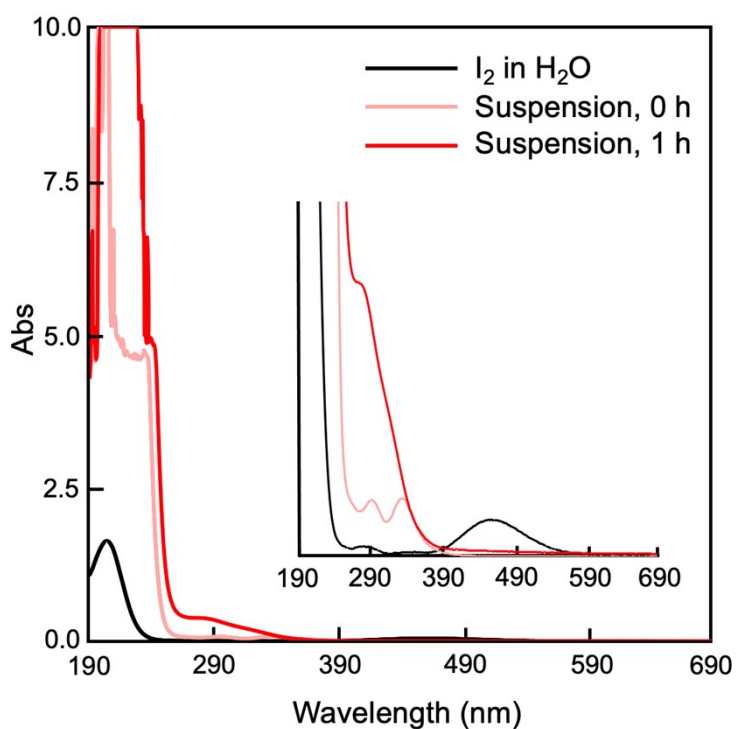


Figure S4. UV-vis absorption spectra of I_2 (black line) and polymerization suspension at 30 °C for 0h (pink line) and 1h (red line). (Conc. 0.65 mM; calculated by iodine group ($-I$) concentration).

Colloid stability of PVAc prepared by *ms* ITP and *ms* CRP

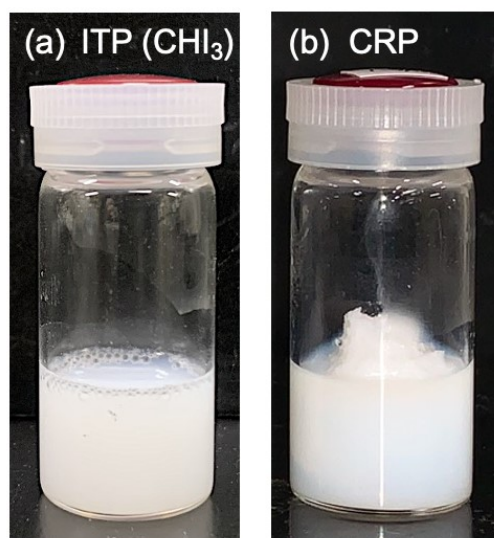


Figure S5. Appearance of PVAc prepared by *ms* ITP for 18 h (a) and *ms* CRP for 8h using V-70 as initiator at 30 °C

Table S6. Zeta potential (ζ) and pH of PVAc prepared by *ms* CRP and *ms* ITP.

Method	<i>ms</i> CRP			<i>ms</i> ITP	
Time	6 h	10 h	after wash	18 h	after wash
pH	6~7	5~6	7	2~3	6~7
ζ (mV)	-4.13	-2.64	-4.67	-1.34	-14.02
State	stable	coagulation	supernatant	suspension	suspension

Alcoholysis of PVAc

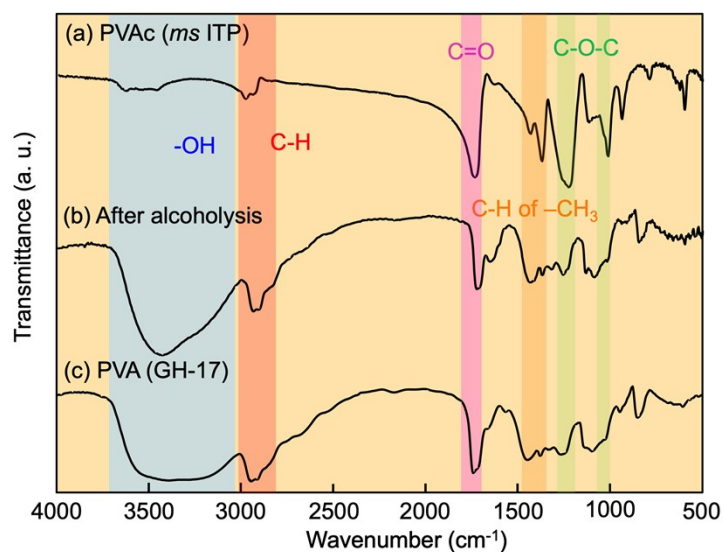


Figure S6. FTIR spectra of PVAc prepared by *ms* ITP before (a) and after (b) alcoholysis, compared with commercial PVA (GH-17) (c).

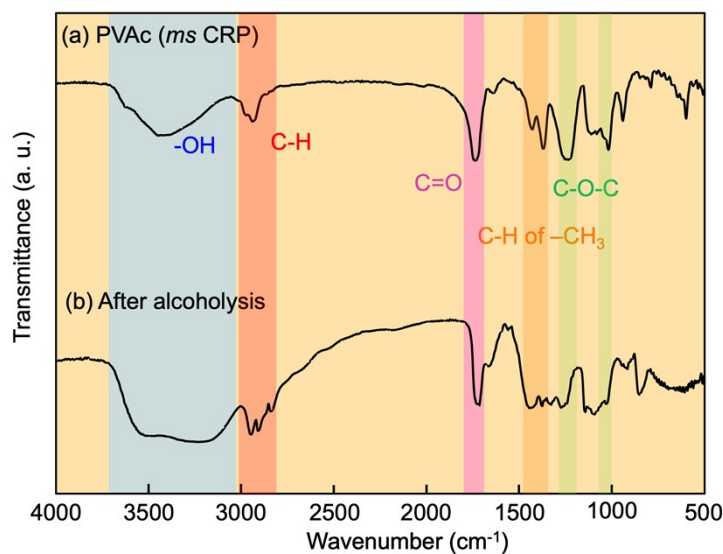


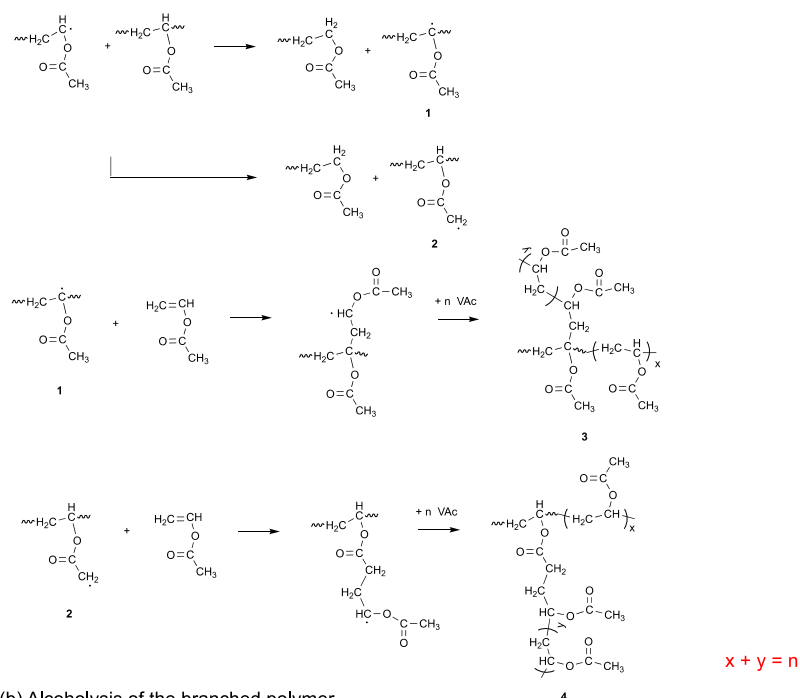
Figure S7. FTIR spectra of PVAc prepared by *ms* CRP before (a) and after (b) alcoholysis.

Table S7. The M_n and M_w/M_n of PVAc prepared by *ms* CRP (a) and *ms* ITP (b) before and after alcoholysis.

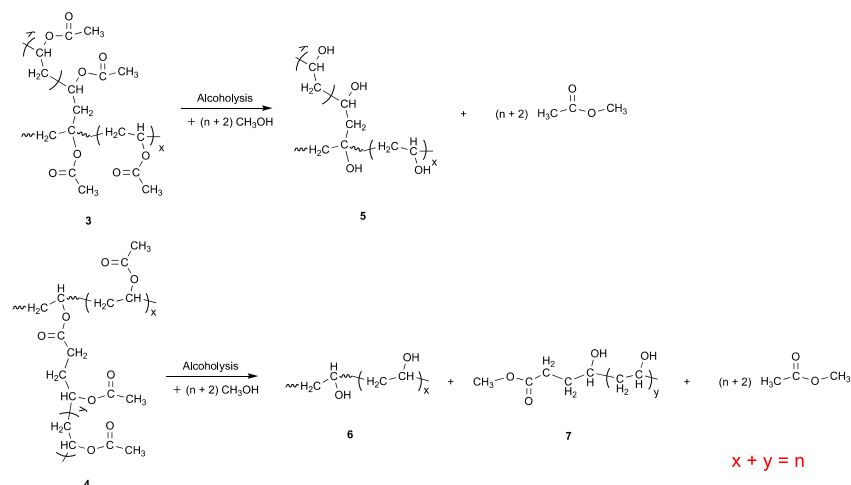
	Before		After	
	M_n	M_w/M_n	M_n	M_w/M_n
<i>ms</i> ITP	22,200	2.41	11,200	1.96
<i>ms</i> CRP	37.7×10^4	4.81	63,800	4.59

Chain transfer to PVAc in *ms* CRP and *ms* ITP of VAc

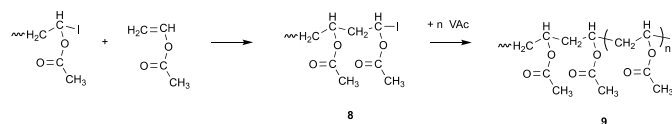
(a) Branching



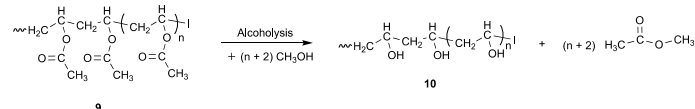
(b) Alcoholysis of the branched polymer



(c) Without branching



(d) Alcoholysis of the polymer without branching



Scheme S2. Mechanisms of the branched PVAc in *ms* CRP (a) and alcoholysis of the branched PVAc (b). Mechanisms of the PVAc without branching in *ms* ITP (c) and alcoholysis of the PVAc without branching (d).

Table S8. The different chain transfer constants to the different positions of polymer.

Position of PVAc	T (°C)	C _{tr}
Methine group ^{a)}	60	3.03 × 10 ⁻⁴
Methyl group of acetoxy substituents ^{a)}	60	1.27 × 10 ⁻⁴
Iodine end group ^{b)}	30	32.98

^{a)} S.-I. Nozakura, Y. Morishima, S. Murahashi, *J. Polym. Sci.*, **1972**, *10*, 2853.

^{b)} Experimental value: using Ethyl iodoacetate as CTA, calculated by eq 4.

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