

Supporting Information

Iodine-influenced morphological evolution of micrometer-sized poly(methyl methacrylate)-*block*-poly(vinyl acetate) particles upon hydrolysis

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Inner morphologies of PMMA and PMMA-*b*-PVAc particles, and PMMA/PVAc composite particles before and after hydrolysis

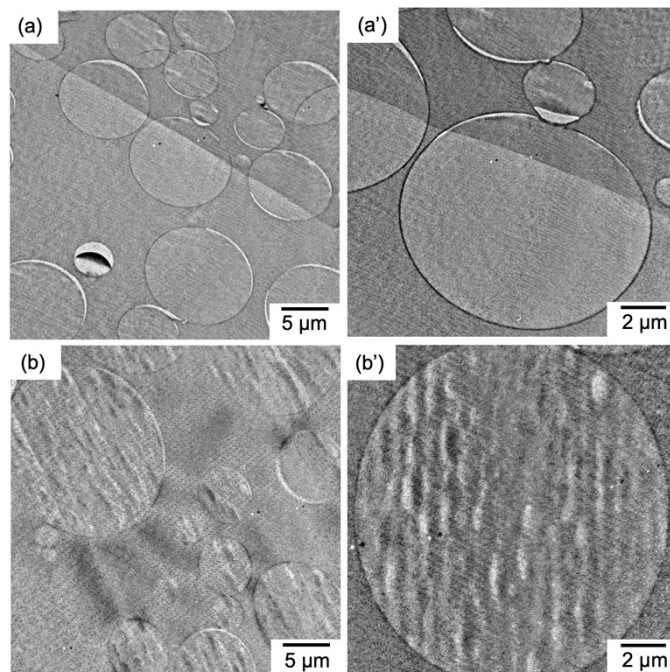


Figure. S1 Internal morphologies of PMMA (a, a') and PMMA-*b*-PVAc particles (b, b').

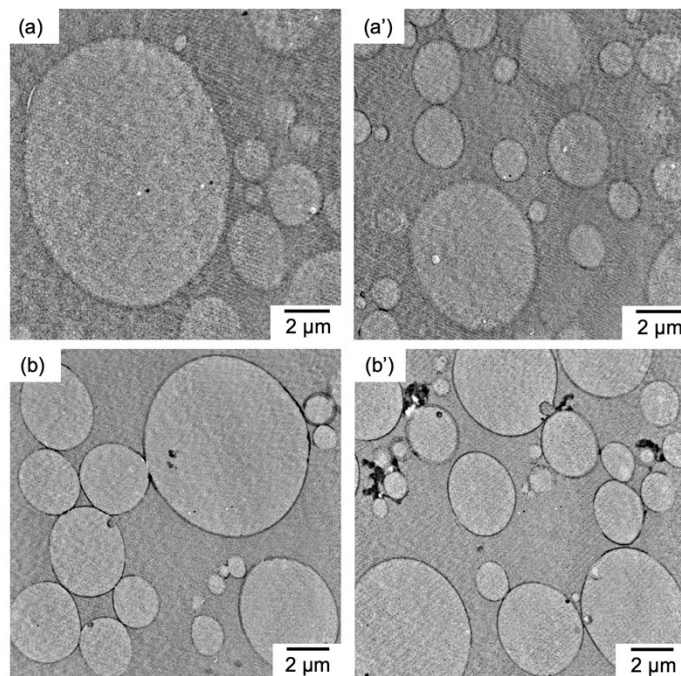


Figure. S2 Inner morphologies of PMMA/PVAc composite particles before (a, a') and after (b, b') hydrolysis.

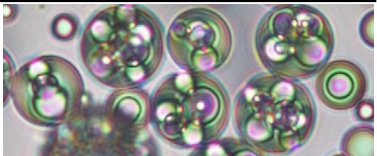

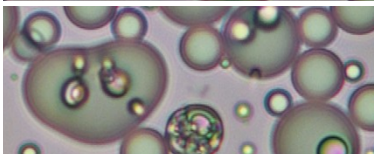
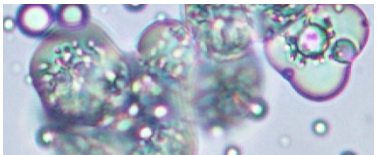
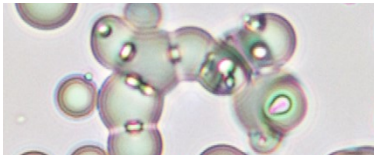
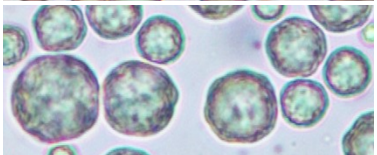
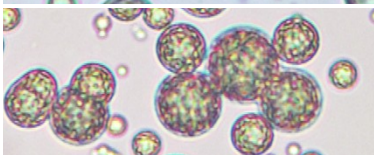
The molecular and morphological characteristics of the series of PMMA-*b*-PVA

Table. S1 The molecular weight, theoretical molecular weight and molecular weight distributions of the series of PMMA-*b*-PVA that were obtained after hydrolyzation.

Sample	DP _{V_A} /DP _{MMA} ^a	M _n (g/mol)	M _{n,th} (g/mol)	Peak M _n (g/mol)	M _w /M _n
1	6/123	14,900	14,900	16,300	1.20
2	9/149	15,700	15,600	19,200	1.35
3	11/149	15,700	15,700	20,100	1.44
4	11/136	14,600	14,200	17,300	1.34
5	15/175	18,900	18,400	24,700	1.73
6	13/136	14,400	14,300	17,700	1.48
7	17/175	18,500	18,500	24,700	1.47

^a After hydrolysis, the units of PVAc were all converted to the units of PVA

Table. S2 The morphological characteristics after hydrolysis of the series of PMMA-*b*-PVA that were obtained after hydrolyzation.

Sample	DP _{VAc} /DP _{MMA} ^a	Morphology ^b	V _{PVA} ^{c, d} (nm ³)	$\frac{V_{PMMA}}{V_{PVA}}$ ^e	OM
1	6/123	SHP	0.36	49	
2	9/149	SHP	0.56	38	
3	11/149	SHP	0.68	31	
4	11/136	MH	0.68	28	
5	15/175	MH	0.92	27	
6	13/136	SHS	0.80	24	
7	17/175	SHS	1.04	24	

^a After hydrolysis, the units of PVAc were all converted to the units of PVA

^b $V_{PVA} = M_{n, PVA} / (\rho_{PVA} \cdot N_A)$, V_{PVA} is volume of the PVA block, $M_{n, PVA}$ is the molecular weight of the block of PVA, ρ is the density of PVA: $\rho_{PVA} = 1.19 \text{ g/cm}^3$, N_A is Avogadro constant.

^c O. Tcherkasskaya, S.-R Ni, and M. A. Winnik, *Macromolecules.*, **29**(12), 4241-4246, 1996.

^d $\rho_{\text{PMMA}} = 1.18 \text{ g/cm}^3$, $V_{\text{MMA}}/V_{\text{VA}}$ relates to the packing coordinate parameter

^e SHP for spherical particles with hollows in the particle, MH for multipods with hollows, SHS for spherical particles with hollows near the surface

Side reactions between iodine radicals and PVAc block in an aqueous medium

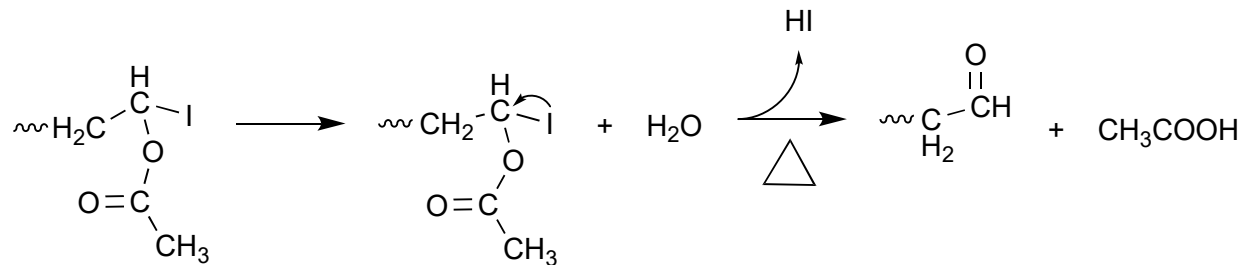
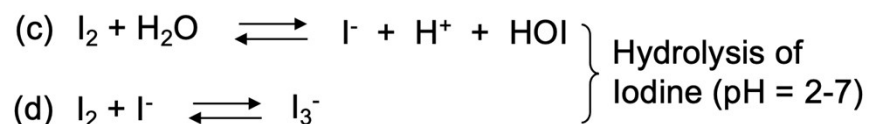
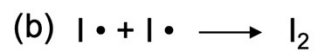
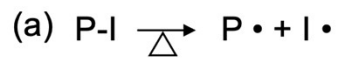


Figure. S3 Side reaction of the loss of iodine ends in *sm*s ITP of VAc.



} Hydrolysis of
Iodine (pH = 2-7)

Figure. S4 Side reactions of the generation of iodic ions.

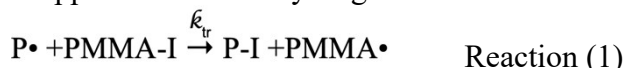
Comparison of the rate of deactivation and the rate of hydrolysis of iodine

In the previous work, it has been displayed that the chain transfer constant (C_{tr}) could be calculated experimentally in the form of conversion by equation (1).¹

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

The p and q represent the conversion of macrochain transfer agent (PMMA-I) and monomer, respectively. However, this time because of the extremely strict condition requested to obtain the direct data from GC, the C_{tr} of 2.6 was selected, which was given in the work of C. Boyer et al.² By utilizing this equation, the remained concentration of the macro chain transfer agent ($1-p$) could be calculated easily.

The main chain transfer appeared in the early stage of *sms* ITP showed as below:

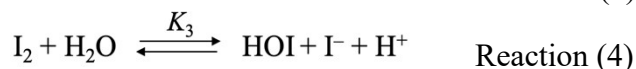


As revealed, the consumption of the PMMA-I within the period (t) based on reaction (1) can be calculated by equation (2) through the following mathematical procedures.

$$\begin{aligned} \text{Consumption of [PMMA-I]} & - \frac{d[\text{PMMA-I}]}{dt} = \hat{k}_{tr} [P\bullet][\text{PMMA-I}] \implies - \frac{d[\text{PMMA-I}]}{[\text{PMMA-I}]} = \hat{k}_{tr} [P\bullet] dt \\ \Downarrow \\ \text{Integration} & - \int_{[\text{PMMA-I}]_0}^{[\text{PMMA-I}]_t} \frac{d[\text{PMMA-I}]}{[\text{PMMA-I}]} = \int_0^t \hat{k}_{tr} [P\bullet] dt \implies \ln\left(\frac{[\text{PMMA-I}]_0}{[\text{PMMA-I}]_t}\right) = \hat{k}_{tr} [P\bullet] t \end{aligned} \quad \text{eq (2)}$$

After taking the original and remained concentrations of PMMA-I into the mathematical model, it is possible to get the theoretical concentration of the polymer radicals.

The free iodine radicals are probably to regenerate the dormant species with these polymer radicals, meanwhile, combining with the other iodine radicals and reacting with water. The deactivation of a polymer radical with an iodine radical ($I\bullet$) and the combination of the two iodine radicals are shown as reaction (2) and reaction (3), respectively. The generated iodine molecules undergo the hydrolysis steps, however in the situation of $\text{pH} < 7$, the general reaction is shown as the reaction (4). The rate constants for each reaction are $k_1 = 9.516 \times 10^9$, $k_2 = 5 \times 10^9 \text{ M}^{-1}\text{S}^{-1}$,³ and $K_3 = 5.4 \times 10^{-13} \text{ M}^2$.⁴



The reactions are second-order reactions, therefore, the generation of deactive polymer (P-I), iodine molecules (I_2), and iodine ions (I^-) within the period (t) based on reaction (2-4) can be calculated by equation (3-5), respectively.

$$[P-I]_t = \hat{k}_1 [P\bullet][I\bullet]t \quad \text{eq (3)}$$

$$[I_2]_t = \hat{k}_2 [I\bullet]^2 t \quad \text{eq (4)}$$

$$[I^-]_t = K_3 [I \bullet] [H_2O]_t \quad \text{eq (5)}$$

To determine whether the regeneration of P-I or the hydrolysis of iodine dominates the procedure at an exact point in time, a comparison between them is represented through the following mathematical equation (6). The original input experimental data are given in Table. S3.

$$\frac{[P-I]_t}{[I^-]_t} = \frac{\bar{k}_1 [P \bullet]_t}{\bar{k}_2 K_3 [I \bullet] [H_2O]_t} \quad \text{eq (6)}$$

After inputting the data of the instantaneous conversion of monomer (6.9 and 11.4 % after 24-hour and 48-hour polymerization, respectively) and the concentration of water (55.55 M L⁻¹), the eq (6) can be simplified with numerical values in Table. S3.

Meanwhile, the concentration of iodide ions ([I⁻]) is calculated through the measurement of pH. It is under the assumption that all hydrogen cations (H⁺) are derived from the hydrolysis of iodine. After 24-hour polymerization, the pH of the medium decreased to 3.085, while 2.755 of that after 48-hour polymerization was measured by a pH meter. At that time, the [I⁻]s in the media are about 8.222 × 10⁻⁴ M L⁻¹ after 24 hours and 17.4 × 10⁻⁴ M L⁻¹ after 48 hours. After substituting the values of [PMMA-I]_t and [I⁻] into the eq (6), the number of [I[•]]_t could be calculated. When the volume of water is known, the mole fractions of iodine species could be told through eq (7-10).

$$n_{[I, \text{all}]} = [PMMA-I]_0 \times V_{H_2O} \quad \text{eq (7)}$$

$$n_{[PMMA-I]_t} = [PMMA-I]_t \times V_{H_2O} \quad \text{eq (8)}$$

$$n_{[I \bullet, \text{th}]_t} = [I \bullet] \times V_{H_2O} \quad \text{eq (9)}$$

$$n_{[I^-]} = [I^-] \times V_{H_2O} \quad \text{eq (10)}$$

The $n_{[I, \text{all}]}$, $n_{[I \bullet, \text{th}]_t}$, $n_{[PMMA-I]_t}$, and $n_{[I^-]}$ represent the mole fraction of the total amount of iodine, the calculated I[•] in the polymerization, the iodine end group, and the I⁻, respectively.

If the regeneration of P-I is superior to the hydrolysis of iodine, the sum of $n_{[I \bullet, \text{th}]_t}$, $n_{[PMMA-I]_t}$, and $n_{[I^-]}$ should be less than or equal to the amount of $n_{[I, \text{all}]}$. But, the data shows that the present sum of $n_{[I \bullet, \text{th}]_t}$, $n_{[PMMA-I]_t}$, and $n_{[I^-]}$ is higher than $n_{[I, \text{all}]}$. Additionally, the number of dropped iodine end groups is much lower than the number of I⁻. Both indicate that the instantaneous [I[•]] leaving from PMMA-I is higher than the theoretic value and the hydrolysis of iodine occurs prior to the regeneration of P-I.

Table. S3 Values of parameters for calculation of iodine species.

<i>Coefficient</i>	<i>eq for polymn of 24h</i>	<i>eq for polymn of 48h</i>
C_{tr}	2.6 ^a	2.6 ^a
q	0.069	0.114
p	0.1696	0.2670
$[PMMA - I]_0$ (mmol/L)	3.6714	4.6176
$[PMMA - I]_t$ (mmol/L)	$= [PMMA - I]_0 \times (1-p)$ $= 3.0486$	$= [PMMA - I]_0 \times (1-p)$ $= 3.3709$
k_p (M ⁻¹ s ⁻¹)	$= 2.43 \times 10^8 \exp(-30600/RT)$ ^{b)} $R=8.314J K^{-1}mol^{-1}$	$= 2.43 \times 10^8 \exp(-30600/RT)$ ^{b)} $R=8.314J K^{-1}mol^{-1}$
$k_{tr, PMMA-I}$ (M ⁻¹ s ⁻¹)	$= C_{tr} \times k_p = 3371$	$= C_{tr} \times k_p = 3371$
$[P\bullet]$ ($\times 10^{-7}$ mmol/L)	6.3824	5.4024
$[P - I]/[I\bullet]$	$1/ 2.134 \times 10^3 \times [I\bullet]$	$1/ 0.903 \times 10^3 \times [I\bullet]$
$[I\bullet]$ ($\times 10^{-1}$ mmol/L)	1.264	5.716
$n_{[I, all]}$ ($\times 10^{-4}$ mmol)	9.413	9.711
$n_{[PMMA-I]_t}$ ($\times 10^{-4}$ mmol)	7.816	7.089
$n_{[I\bullet, th]}$ ($\times 10^{-4}$ mmol)	0.324	1.211
$n_{[I^-]}$ ($\times 10^{-4}$ mmol)	2.108	3.659
$[I^-]$ ($\times 10^{-1}$ mmol/L)	8.222	17.40
V_{H_2O} ($\times 10^{-4}$ L)	2.564	2.103
$[H_2O]$ (mol/L)	55.55	55.55

a) C. Boyer, P. Lacroix-Desmazes, J.-J. Robin, B. Boutevin, *Macromolecules*, **2006**, *39*, 4044

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

Comparison of the performances between PMMA and PMMA-*b*-PVAc

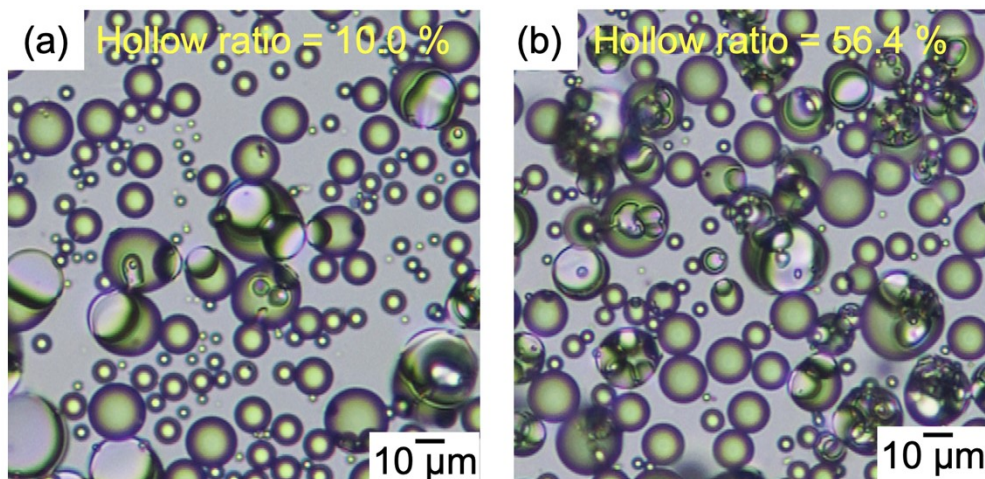


Figure. S5 Optical images of PMMA-*b*-PVAc particles after hydrolyzed at 70°C (a) and 125°C (b), respectively. (Hollow ratio (%) = the number of particles with hollow structures/the number of particles in an optical micrograph \times 100)

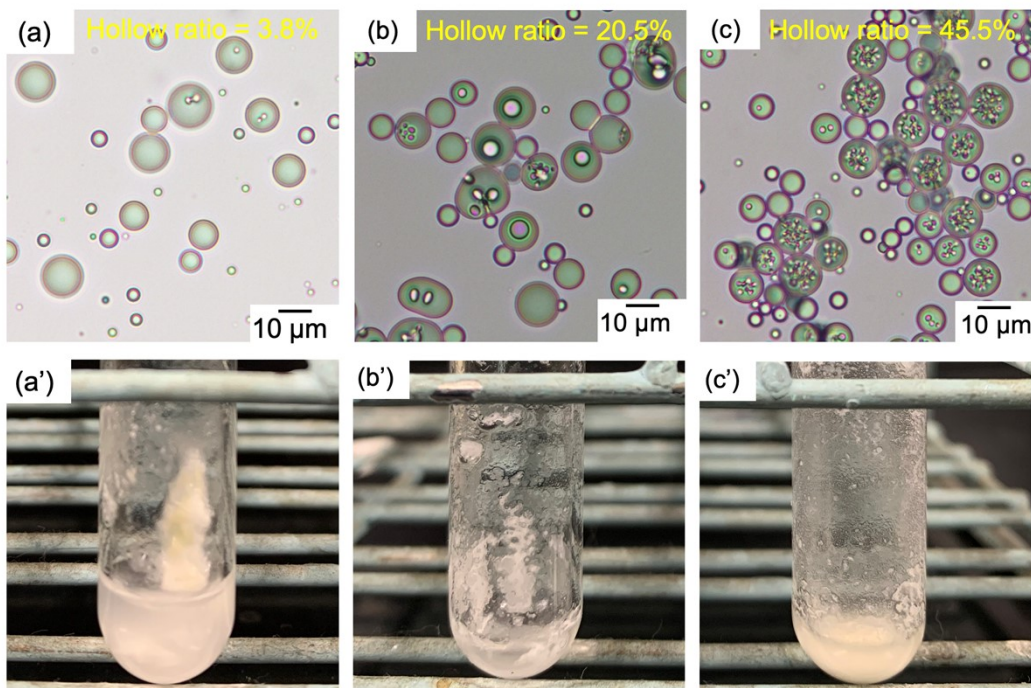


Figure. S6 Optical images (a-c) and appearances (a'-c') of PMMA particles (a, a', b, b'), which before hydrolysis were treated without (a, a') and with (b, b') the swelling process of toluene, and swollen PMMA-*b*-PVAc (c, c') particles after hydrolysis. (Hollow ratio (%) = the number of particles with hollow structures/the number of particles in an optical micrograph \times 100)

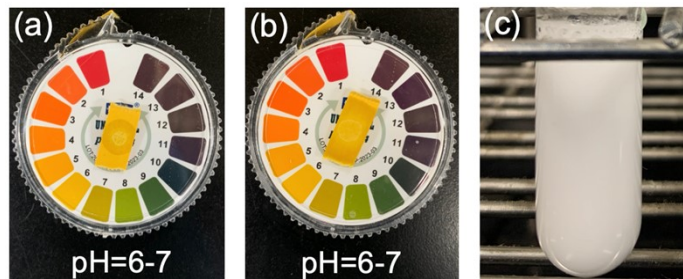


Figure. S7 pH tested by pH paper before (a) and after (b) the same treatment of PMMA-I as *sms* ITP but without VAc, and appearance of suspension (c) after treatment.

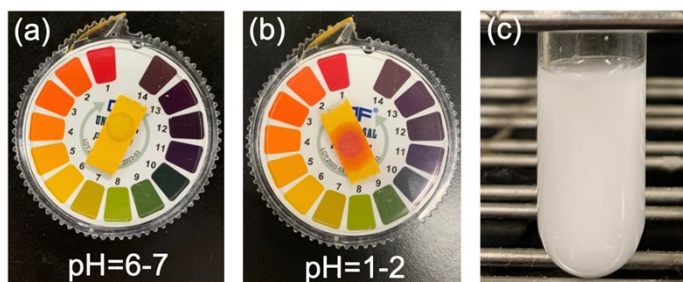


Figure. S8 pH tested by pH paper before (a) and after (b) *sms* ITP of VAc, and appearance of suspension (c) after *sms* ITP.

PMMA-*b*-PVA with the same DP of PVA

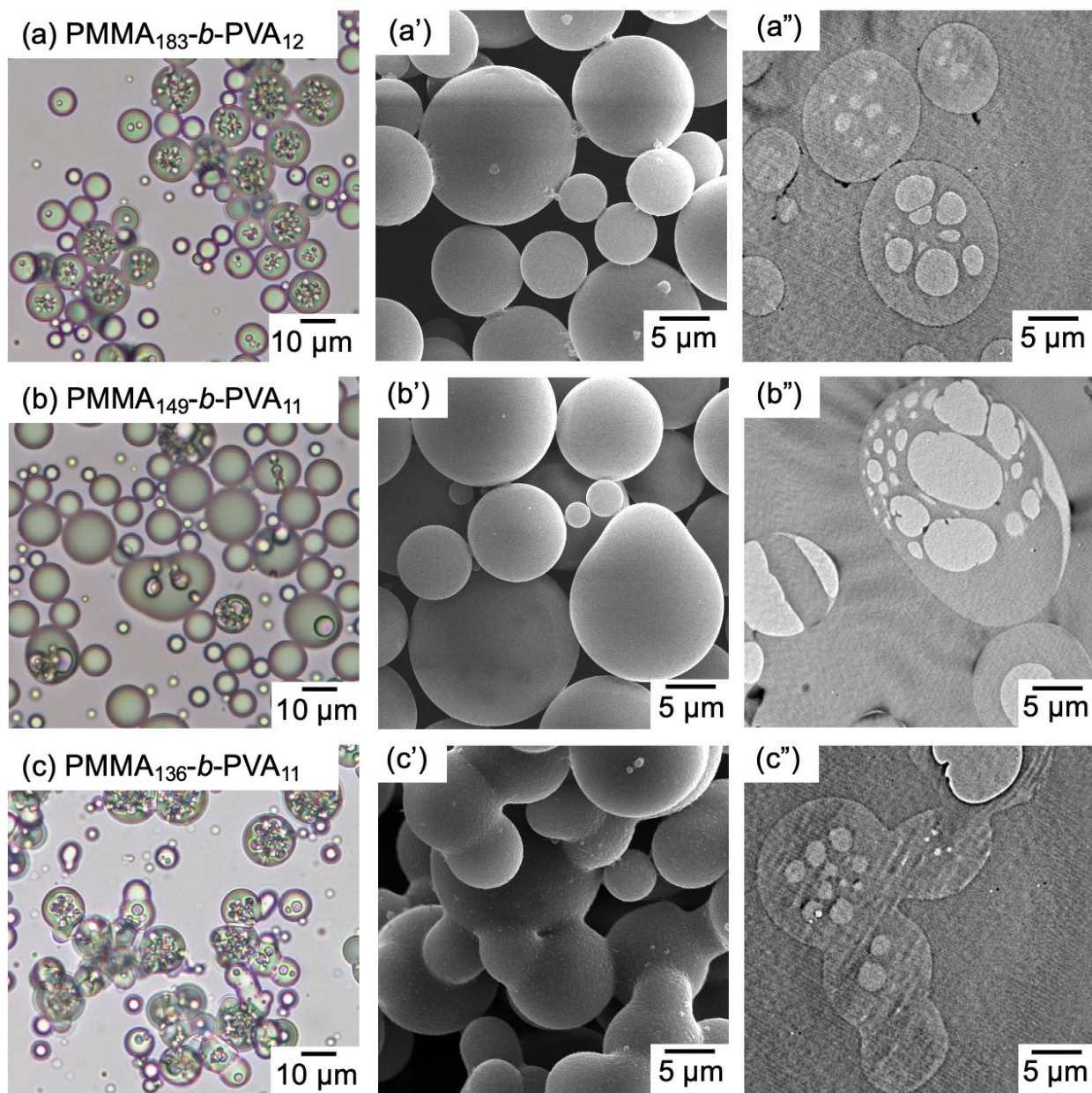


Figure. S9 Optical (a-c), SEM (a'- c') and cross-sectional (a''-c'') images of the PMMA-*b*-PVA particles which hydrolyzed from PMMA-*b*-PVAc with same DP_{VAc} , but different ratio of DP_{VAc}/DP_{MMA} : PMMA₁₈₃-*b*-PVA₁₂, $DP_{VAc}/DP_{MMA} = 0.066$ (a-a''), PMMA₁₄₉-*b*-PVA₁₁, $DP_{VAc}/DP_{MMA} = 0.074$ (b-b''), and PMMA₁₃₆-*b*-PVA₁₁, $DP_{VAc}/DP_{MMA} = 0.081$ (c-c'').

Comparison of particle stability between SHP and MH

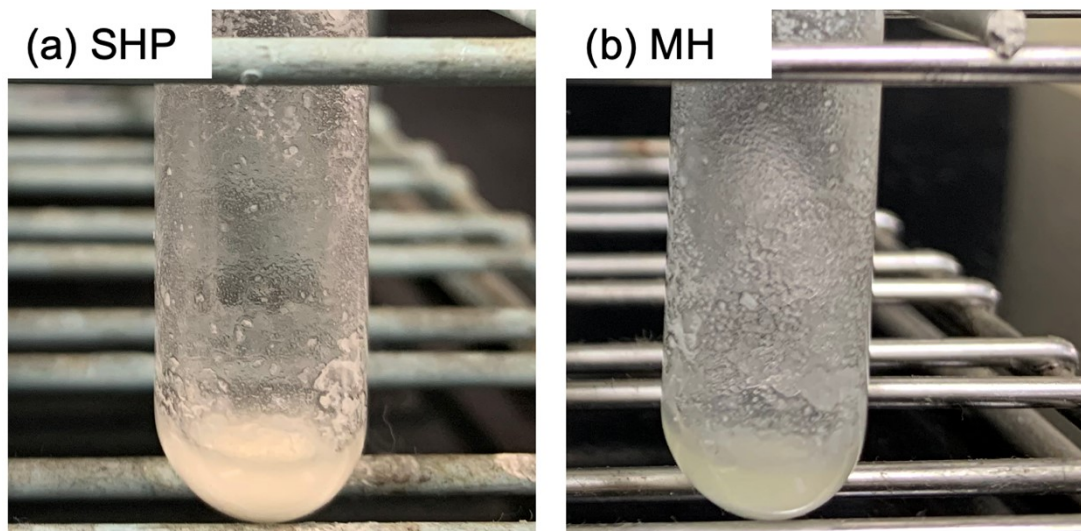
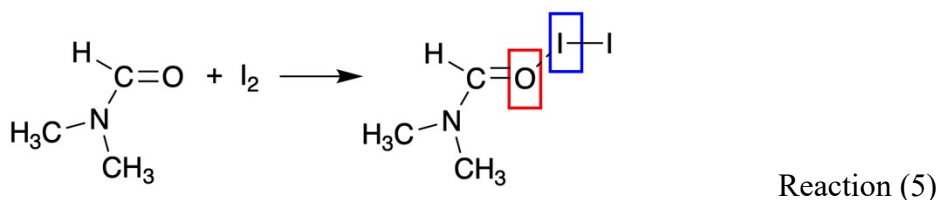


Figure. S10 Appearances (a, b) of particle stability of different PMMA-*b*-PVAcS after hydrolysis showing the morphology of SHP (a) and MH (b), respectively.

Calculation of carrying rate of iodine end groups

The UV-Vis was used to calculate the carrying rate of the iodine end group of polymers after each step. Since the dipole-dipole bond between DMF and the iodine group could be generated by reaction (5), through which the iodine group could drop from the polymer chain.^{5,6} The probable fate of the free iodine groups is the generation of iodine molecules. To make the iodine group drop from the polymer chain completely, the solution of polymer in DMF was treated under UV light for 4 hours and stood for one night.

I₂/DMF complex



For the known data of the measured absorbance intensity of polymer with iodine end (polymer-I) (A_{exp}), the measured absorbance intensity of iodine molecules (A_I), and the concentration of iodine molecules (C_I), it is possible to calculate the concentration of polymer-I ($C_{\text{polymer-I, exp}}$) by equation (11).

$$C_{\text{polymer-I,exp}} = \frac{A_{\text{exp}}}{A_I} \times C_I \times 2 \quad \text{eq (11)}$$

Then, the ratio of the calculated $C_{\text{polymer-I, exp}}$ to the concentration of the weighted polymer ($C_{\text{polymer-I,theo}}$) is defined as the carrying rate of the iodine end group ($R_{\text{iodine end group}}$) (equation (12)).

$$\text{Carrying rate of iodine end group} = \frac{C_{\text{polymer-I,exp}}}{C_{\text{polymer-I,theo}}} \quad \text{eq (12)}$$

The characteristic peak of I₂ in DMF at 262 nm, which shifted a little due to the influence of the polymer chain, was used to calculate the carrying rate of the iodine end group. It is assumed that the PMMA-*b*-PVAc were hydrolyzed thoroughly to PMMA-*b*-PVA, since the low DP_{VAc}. So, the polymer after hydrolysis is expressed as PMMA-*b*-PVA.

In the situation of SHP, the obtained UV-Vis lines of polymer-I after each step are depicted in Fig. S11, and the obtained value of the carrying rate is shown in Table.S4. While in the situation of MH, the data are shown in Fig. S12 and Table. S5, respectively.

Comparison of carrying rate of iodine end groups in the case of SHP and MH

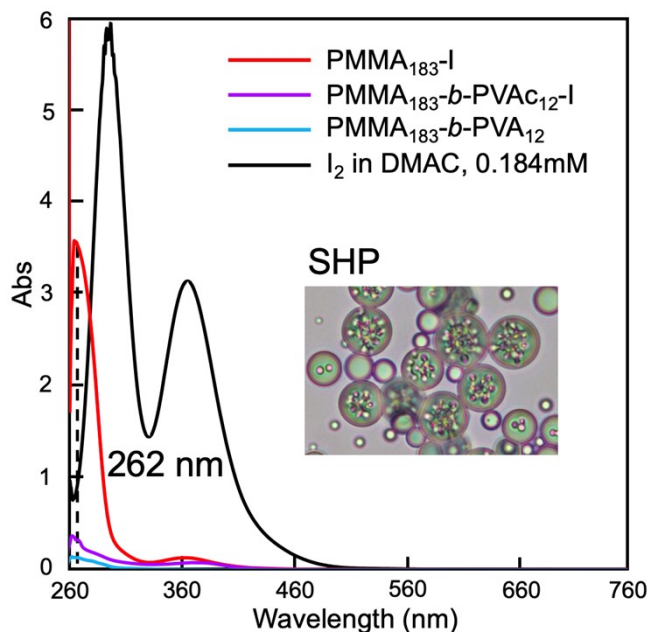


Figure. S11 UV-vis of PMMA-I (red line), PMMA-*b*-PVAc-I before (purple line) and after (blue line) hydrolysis, prepared with $DP_{MMA} = 183$ and $DP_{Vac} = 12$, which showed the morphology of SHP after hydrolysis. All of the lines were compared with I_2 (black line). $[I_2] = 1.084 \times 10^{-1}$ mM.

Table. S4 The theoretical concentration of polymer with iodine end ($C_{\text{polymer-I,theo}}$), the measured concentration of polymer with iodine end ($C_{\text{polymer-I,exp}}$), and the calculated value of carrying rate of iodine end groups ($R_{\text{iodine end group}}$) in the case of SHP.

Sample	$C_{\text{polymer-I,theo}}$ (mmol/L)	$C_{\text{polymer-I,exp}}$ (mmol/L)	Carrying rate of iodine end groups ($R_{\text{iodine end group}}$, %)
PMMA ₁₈₃ -I	0.145	0.2200	100.0
PMMA ₁₈₃ - <i>b</i> -PVAc ₁₂ -I	0.122	0.0354	29.0
PMMA ₁₈₃ - <i>b</i> -PVA ₁₂	0.012	0.0089	74.2

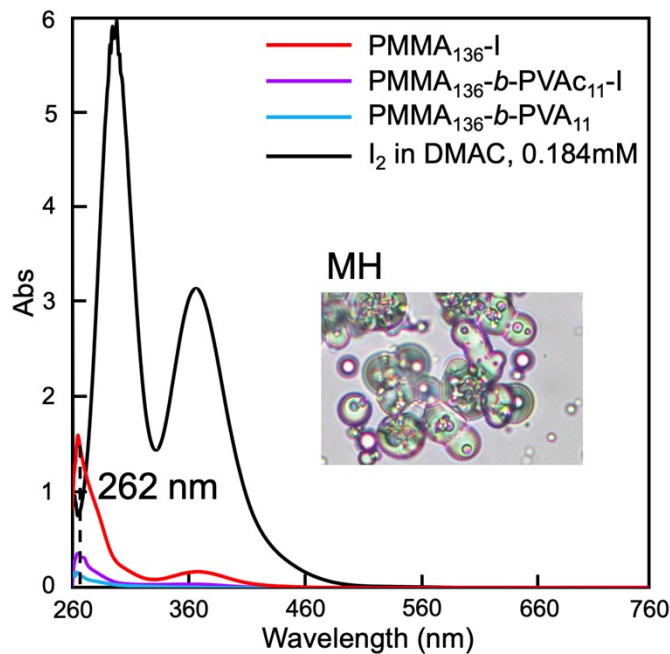


Figure. S12 UV-vis of PMMA-I (red line), PMMA-*b*-PVAc-I before (purple line) and after (blue line) hydrolysis, prepared with $DP_{MMA} = 136$ and $DP_{VAc} = 11$, which showed the morphology of MH after hydrolysis. All of the lines were compared with I_2 (black line). $[I_2] = 1.084 \times 10^{-1}$ mM.

Table. S5 The theoretical concentration of polymer with iodine end ($C_{\text{polymer-I,theo}}$), the measured concentration of polymer with iodine end ($C_{\text{polymer-I,exp}}$), and the calculated value of carrying rate of iodine end groups ($R_{\text{iodine end group}}$) in the case of MH.

Sample	$C_{\text{polymer-I,theo}}$ (mmol/L)	$C_{\text{polymer-I,exp}}$ (mmol/L)	Carrying rate of iodine end groups ($R_{\text{iodine end group}}$, %)
PMMA ₁₃₆ -I	0.154	0.1000	65.0
PMMA ₁₃₆ - <i>b</i> -PVAc ₁₁ -I	0.090	0.0231	25.7
PMMA ₁₃₆ - <i>b</i> -PVA ₁₁	0.006	0.005	88.3

The concentration of iodine ions after hydrolysis

According to the carrying rate of iodine end groups, the amount of lost iodine ends in the step of hydrolysis could be calculated, based on the following equations (eq (13-15)).

$$n_{\text{iodine end, before}} = \frac{W_{\text{PMMA-}b\text{-PVAc}}}{M_{n, \text{PMMA-}b\text{-PVAc}}} \times R_{\text{iodine end group of PMMA-}b\text{-PVAc}} \quad \text{eq (13)}$$

$$n_{\text{iodine end, after}} = n_{\text{iodine end, before}} \times R_{\text{iodine end group of PMMA-}b\text{-PVA}} \quad \text{eq (14)}$$

$$n_{\text{lost iodine end}} = n_{\text{iodine end, before}} - n_{\text{iodine end, after}} \quad \text{eq (15)}$$

In these equations, the $n_{\text{iodine end, before}}$ and $n_{\text{iodine end, after}}$ refer to the molar fraction of iodine end of PMMA-*b*-PVAc and PMMA-*b*-PVA, respectively, which are equal to the molar fraction of polymer with iodine end before and after hydrolysis. So, the $n_{\text{lost iodine end}}$, which refers to the molar fraction of the lost iodine end after hydrolysis, could be equal to the difference between $n_{\text{iodine end, before}}$ and $n_{\text{iodine end, after}}$. The $W_{\text{PMMA-}b\text{-PVAc}}$ and $M_{n, \text{PMMA-}b\text{-PVAc}}$ represent the weight of PMMA-*b*-PVAc used in hydrolysis and the measured molecular weight of PMMA-*b*-PVAc, respectively.

The dropped iodine end groups probably underwent the reaction between iodine and water, resulting in the generation of iodine ions. Therefore, it is supposed that all dropped iodine end groups convert into the iodine ions in the process of hydrolysis. The $n_{\text{lost iodine end}}$ divided by the volume of water (V_{water}) is equivalent to the concentration of iodine ions ($C_{\text{iodine ions}}$), as the mathematical procedure of equation (16). The values of $C_{\text{iodine ions}}$ calculated in both cases of SHP and MH are shown in Table. S6.

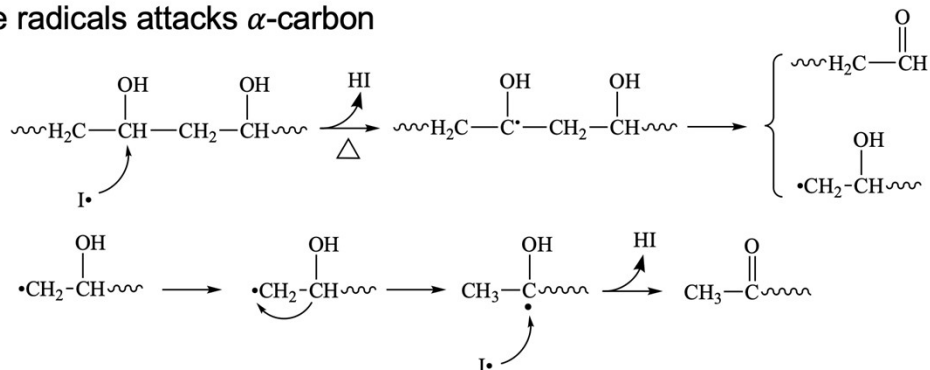
$$C_{\text{iodine ions}} = \frac{n_{\text{lost iodine end}}}{V_{\text{water}}} \quad \text{eq (16)}$$

Table. S6 The molar fractions of iodine end groups before and after hydrolysis ($n_{\text{iodine end, before}}$ and $n_{\text{iodine end, after}}$), the molar fractions of lost iodine end ($n_{\text{lost iodine end}}$), and the calculated concentrations of iodine ions ($C_{\text{iodine ions}}$) in the case of SHP and MH, respectively.

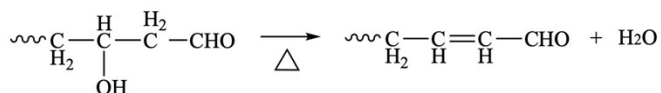
Sample	$n_{\text{iodine end, before}}$ (mmol $\times 10^{-3}$)	$n_{\text{iodine end, after}}$ (mmol $\times 10^{-3}$)	$n_{\text{lost iodine end}}$ (mmol $\times 10^{-3}$)	$C_{\text{iodine ions}}$ (mmol/L)	Morphology
PMMA ₁₈₃ - <i>b</i> -PVAc ₁₂	0.222	0.165	0.057	0.358	SHP
PMMA ₁₃₆ - <i>b</i> -PVAc ₁₁	0.262	0.231	0.031	0.168	MH

Crosslinking structure appeared in the case of SHS

(a) Iodine radicals attacks α -carbon



(b) Aldol condensation



(c) Crosslinking structure

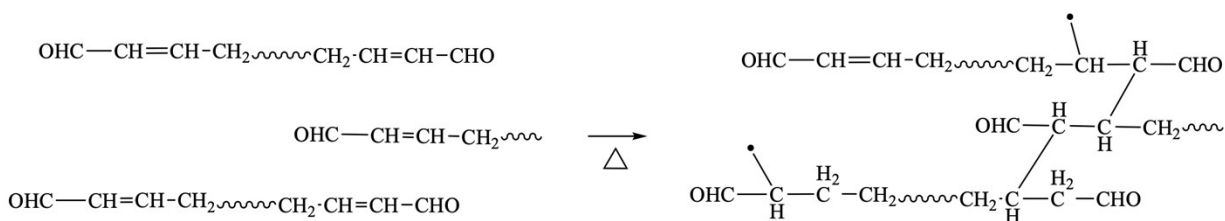


Figure. S13 (a) degradation of PVA in the presence of free iodine radicals, (b) aldol reaction of aldehyde-terminated polymers, and (c) crosslinking reaction between aldol-condensed polymers.

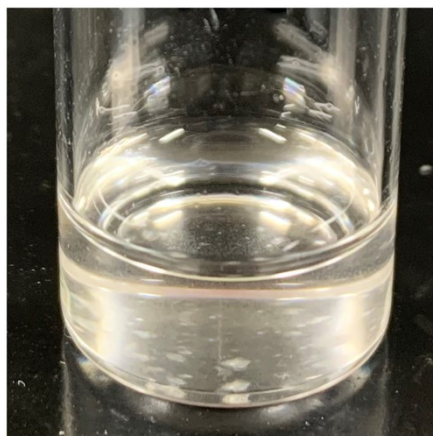


Figure. S14 The unsolved polymer after hydrolysis stands in DMF for 24 hours when the DP_{VAc}/DP_{MMA} of PMMA-*b*-PVAc is higher than 0.096.

Comparison of Carrying rate and amount of iodine end groups at $DP_{VAc}/DP_{MMA} > 0.096$

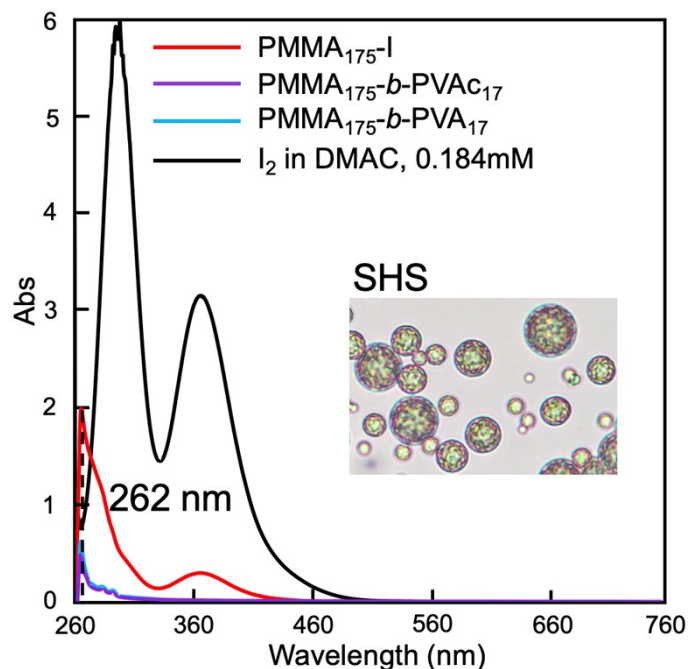


Figure. S15 UV-vis of PMMA-I (red line), PMMA-*b*-PVAc-I before (purple line) and after (blue line) hydrolysis, prepared with $DP_{MMA} = 175$ and $DP_{VAc} = 17$, which showed the morphology of SHS after hydrolysis. All of the lines were compared with I_2 (black line). $[I_2] = 1.084 \times 10^{-1}$ mM.

Table. S7 The theoretical concentration of polymer with iodine end ($C_{\text{polymer-I,theo}}$), the measured concentration of polymer with iodine end ($C_{\text{polymer-I,exp}}$), and the calculated value of carrying rate of iodine end groups ($R_{\text{iodine end group}}$) in the case of SHS.

Sample	$C_{\text{polymer-I,theo}}$ (mmol/L)	$C_{\text{polymer-I,exp}}$ (mmol/L)	Carrying rate of iodine end groups ($R_{\text{iodine end group}}$, %)
PMMA ₁₇₅ -I	0.141	0.1302	92.2
PMMA ₁₇₅ - <i>b</i> -PVAc ₁₇ -I	0.042	0.0282	67.1
PMMA ₁₇₅ - <i>b</i> -PVA ₁₇	0.077	0.0393	51.0

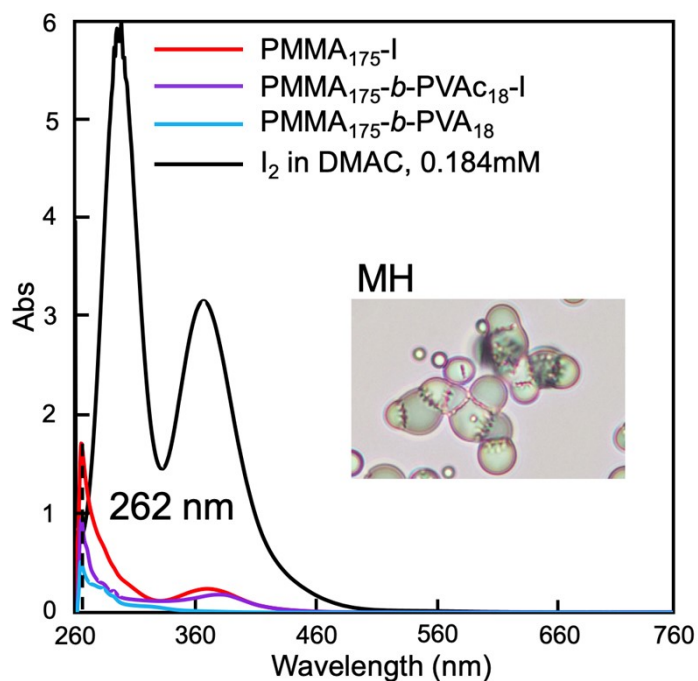


Figure. S16 UV-vis of PMMA-I (red line), PMMA-*b*-PVAc-I before (purple line) and after (blue line) hydrolysis, prepared with $DP_{MMA} = 175$ and $DP_{VAc} = 18$, which showed the morphology of MH after hydrolysis. All of the lines were compared with I_2 (black line). $[I_2] = 1.084 \times 10^{-1}$ mM.

Table. S8 The theoretical concentration of polymer with iodine end ($C_{\text{polymer-I,theo}}$), the measured concentration of polymer with iodine end ($C_{\text{polymer-I,exp}}$), and the calculated value of carrying rate of iodine end groups ($R_{\text{iodine end group}}$) in the case of MH, when the PMMA-*b*-PVAc prepared with a high ratio of DP_{VAc}/DP_{MMA} .

Sample	$C_{\text{polymer-I,theo}}$ (mmol/L)	$C_{\text{polymer-I,exp}}$ (mmol/L)	Carrying rate of iodine end groups
PMMA ₁₇₅ -I	0.154	0.1060	68.9
PMMA ₁₇₅ - <i>b</i> -PVAc ₁₈ -I	0.086	0.0588	47.0
PMMA ₁₇₅ - <i>b</i> -PVA ₁₈	0.052	0.0319	61.3

Table. S9 The molar fractions of iodine end groups before and after hydrolysis ($n_{\text{iodine end, before}}$ and $n_{\text{iodine end, after}}$), the molar fractions of lost iodine end ($n_{\text{lost iodine end}}$) in the case of SHS and MH, respectively.

Sample	$n_{\text{iodine end, before}}$ (mmol $\times 10^{-3}$)	$n_{\text{iodine end, after}}$ (mmol $\times 10^{-3}$)	$n_{\text{lost iodine end}}$ (mmol $\times 10^{-3}$)	Morphology
PMMA ₁₇₅ - <i>b</i> -PVA _{c17}	0.453	0.231	0.222	SHS
PMMA ₁₇₅ - <i>b</i> -PVA _{c18}	0.406	0.249	0.157	MH

Synthesis of PMMA/PVAc composite particles

Synthesis of PMMA by dispersion polymerization⁷

PVP (0.6 g), MMA (4 g), and AIBN (0.04 g) were dissolved orderly in the cosolvent of methanol (16.8 g) and water (7.2 g). Subsequently, the monomer solution was evenly divided into four glass tubes, which were sealed off after being degassed ten times with vacuum/N₂ gas cycles and covered with aluminum foil. Finally, the polymerization was conducted at 60 °C for 24 h with a horizontal shaking rate of 80 rpm. The PMMA particles were collected after being centrifuged three times by water at 8000 rpm, 20 °C, and 10 min.

Synthesis of PVAc⁸

The PVAc was synthesized by microsuspension conventional radical polymerization (*ms* CRP). V-70 (0.03 g) was dissolved in VAc (3 g). Next, the mixture was poured into an aqueous phase consisting of a 1 wt% PVA aqueous solution (27 g). After homogenizing for 5 min using a homogenizer (ABM-2, Nihonseiki Kaisha, Ltd., Japan) at 3,700 rpm, a monomer dispersion was obtained. Subsequently, the monomer dispersion was evenly divided into four glass tubes, which were sealed off after being degassed five times with vacuum/N₂ gas cycles. Finally, *ms* CRP was conducted at 30 °C for 24 h with a horizontal shaking rate of 120 rpm. The polymers were collected after being centrifuged three times with water at 8000 rpm, 5 °C, and 10 min.

Synthesis of PMMA/PVAc composite particles

PMMA (1 g) and PVAc (0.1 g) were dissolved in toluene (1 g), in which the weight ratio of PMMA and PVAc was controlled at 10:1 similar to the ratio of ITP-obtained PMMA-*b*-PVAc. Next, the mixture was poured into an aqueous phase consisting of a 1 wt% PVA aqueous solution (10 g). After homogenizing for 5 min using a homogenizer (ABM-2, Nihonseiki Kaisha, Ltd., Japan) at 4,000 rpm, a suspension of composite particle was obtained. The polymers were collected after being centrifuged three times with water at 8000 rpm, 5 °C, and 10 min.

Synthesis of PMMA-*b*-PVAc particles by two-step RAFT polymerization

Synthesis of micrometer-sized PMMA particles

PMMA was prepared in a molar ratio of [MMA]:[AIBN]:[C₁₁H₁₁NS₂] = 163:0.67:1. PVP (0.6 g), MMA (3 g), AIBN (0.02 g) and 2-cyano-2-propyl benzodithioate (C₁₁H₁₁NS₂, 0.04 g) were dissolved orderly in the cosolvent of methanol (18.9 g) and water (8.1 g). Subsequently, the monomer solution was evenly divided into four glass tubes, which were sealed off after being degassed ten times with vacuum/N₂ gas cycles and covered with aluminum foil. Finally, the polymerization was conducted at 60 °C for 24 h with a horizontal shaking rate of 80 rpm. The PMMA particles were collected after being centrifuged three times by water at 8000 rpm, 20 °C, and 10 min.

Synthesis of micrometer-sized PMMA-*b*-PVAc particles

Micrometer-sized PMMA-*b*-PVAc particles were synthesized by seeded microsuspension RAFT polymerization. An oil phase of V-70 (1.2 mg, 1 wt% relative to monomer), toluene (5 mg, 2 wt% relative to PMMA seeds), and VAc (0.028 g) were mixed with 1 wt% PVA aqueous solution (0.6 g), which was homogenized by a biomixer (NS-52K, Nihonseiki Kaisha, Ltd.) at 6500 rpm for 5 min afterward. Next, the VAc emulsion, which was extracted one-tenth from the above emulsion, was added to the suspension of PMMA particles. The RAFT-obtained PMMA was used as the macrochain transfer agent in this step and expressed as PMMA-X. The suspension of PMMA seeds was prepared in a molar ratio of [VAc]:[V-70]:[PMMA-X] = 50:0.6:1, and the water was adjusted to control the solid content of the total mixture to 10 wt%. Then, the mixture was immersed in an ice bath and stirred by a magnetic stirrer at 150 rpm for 2 h to proceed with the swelling of VAc. Following the swelling, the mixture was evenly divided using four glass tubes and sealed off after being degassed five times with vacuum/N₂ gas cycles. The sealed tubes were placed in a water bath at 30°C for 24 h with a horizontal shaking rate of 80 rpm. PMMA-*b*-PVAc particles were collected by centrifugation conducted in triplicate in water at 8000 rpm for 10 min at 5°C.

References

1. P. Lacroix-Desmazes and J. Tonnar, in *Polymer Science: A Comprehensive Reference*, 2012, DOI: 10.1016/b978-0-444-53349-4.00065-0, pp. 159-180.
2. C. Boyer, P. Lacroix-Desmazes, J. J. Robin and B. Boutevin, *Macromolecules*, 2006, **39**, 4044-4053.
3. L. Wojnarovits and J. A. LaVerne, *Radiat. Phys. Chem.*, 1996, **47**, 99-101.
4. I. Lengyel, I. R. Epstein and K. Kustin, *Inorg. Chem*, 1993, **32**, 5880-5882.
5. X. Liu, L. Zhang, Z. Cheng and X. Zhu, *Polym. Chem.*, 2016, **7**, 3576-3588.
6. C. Schmulbach and R. S. Drago, *J. Am. Chem. Soc.*, 1960, **82**, 4484-4487.
7. M. Okubo, J. Izumi, T. Hosotani and T. Yamashita, *Colloid Polym. Sci.*, 1997, **275**, 797-801.
8. C. Huang, T. Suzuki and H. Minami, *Polym. Chem.*, 2022, **13**, 640-648.