Supporting Information

Toward Alternating Copolymerization of Maleimide and Vinyl Acetate Driven by Hydrogen Bonding

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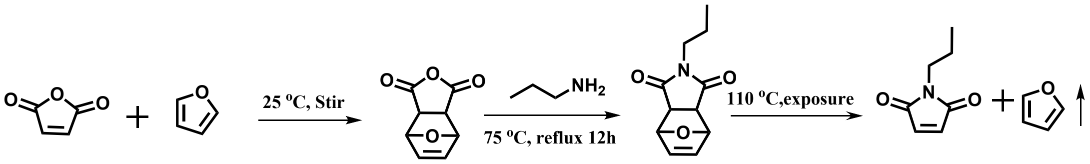


Scheme S1. Synthesis of N-substituted maleimide

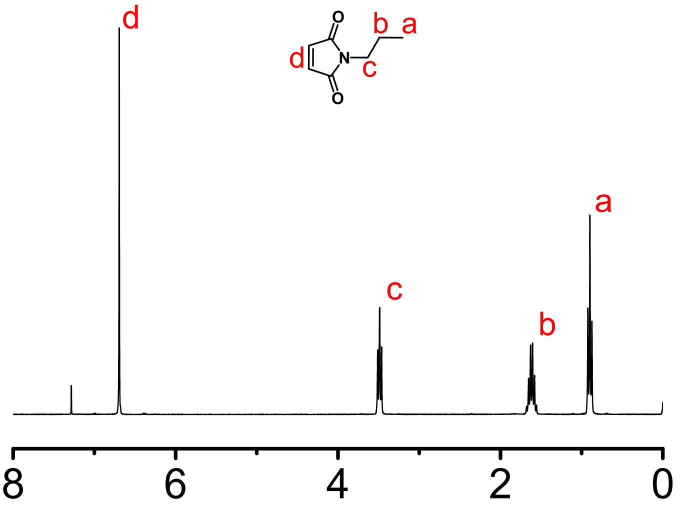


Figure S1. ^{1}H NMR spectra of monomer N-propylmaleimides(MI) in $CDCl_3$

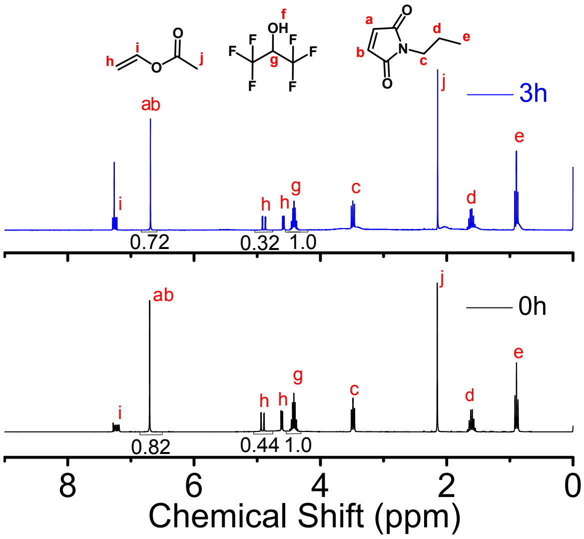


Figure S2. Direct ^{1}H NMR analysis spectra of monomer conversion in $CDCl_3$. The integral of the signal of proton (g) belong to HFIP in the 1H NMR was set to be 1.0, served as internal standard for the decrease of the integral of double bonds belong to each monomer. 0 h and 3 h was toward initial time and the third hour of the whole copolymerization. $\text{Conv.}_{\text{MI}} = I_{6.7,0\text{ h}} - I_{6.7,3\text{ h}} / I_{6.7,0\text{ h}} \times 100\%$; $\text{Conv.}_{\text{VAc}} = I_{4.9,0\text{ h}} - I_{4.9,3\text{ h}} / I_{4.9,0\text{ h}} \times 100\%$; The conversion of monomer at other times is similar to the calculation illustrated above.

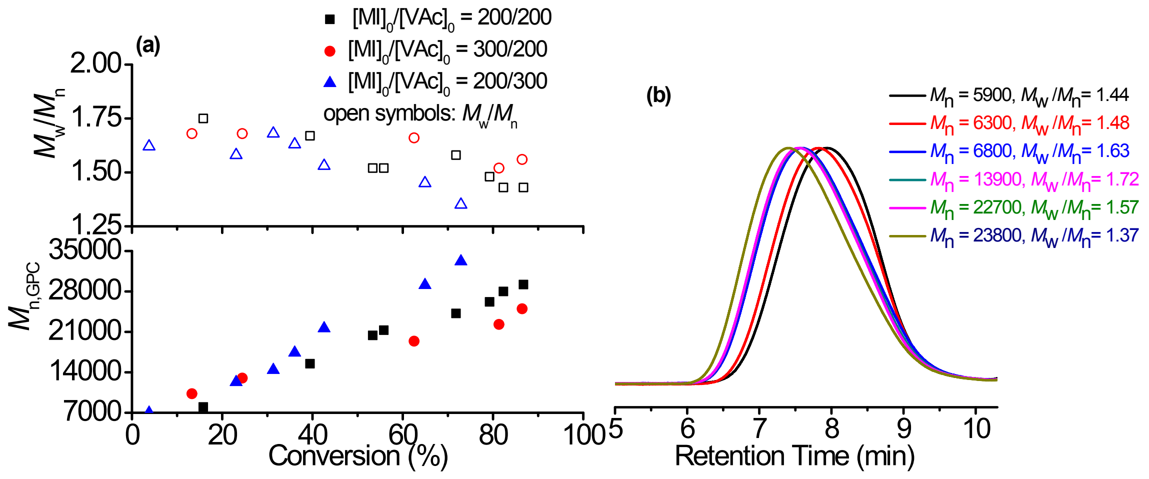
Equation S1.

Normalized chain length $((i\text{-}1)\text{-}i) = (\text{Conv.}_{\text{total}}\,(i\text{-}1) + \text{Conv.}_{\text{total}}\,(i)) / 2\,\text{Conv.}_{\text{max}}$;

Normalized chain length $(i) = \text{Conv.}_{\text{total}}\,(i) / \text{Conv.}_{\text{max}}$;

$F_{\text{cum, VAc}}\,(i) = (200\times\text{Conv.}_{\text{VAc}}) / (200\times\text{Conv.}_{\text{MI}} + 200\times\text{Conv.}_{\text{VAc}})$ ($\text{Conv.}_{\text{max}}$ equal to the maximum value of $\text{Conv.}_{\text{total}}$) ;

$F_{\text{inst, VAc}}\,((i\text{-}1)\text{-}i) = (\text{Conv.}_{\text{total}}\,(i) \times F_{\text{cum, VAc}}\,(i) - \text{Conv.}_{\text{total}}\,(i\text{-}1) \times F_{\text{cum, VAc}}\,(i\text{-}1)) / [(\text{Conv.}_{\text{total}}\,(i) \times F_{\text{cum, VAc}}\,(i) - \text{Conv.}_{\text{total}}\,(i\text{-}1) \times F_{\text{cum, VAc}}\,(i\text{-}1)) + (\text{Conv.}_{\text{total}}\,(i) \times F_{\text{cum, MI}}\,(i) - \text{Conv.}_{\text{total}}\,(i\text{-}1) \times F_{\text{cum, MI}}\,(i\text{-}1))]$.



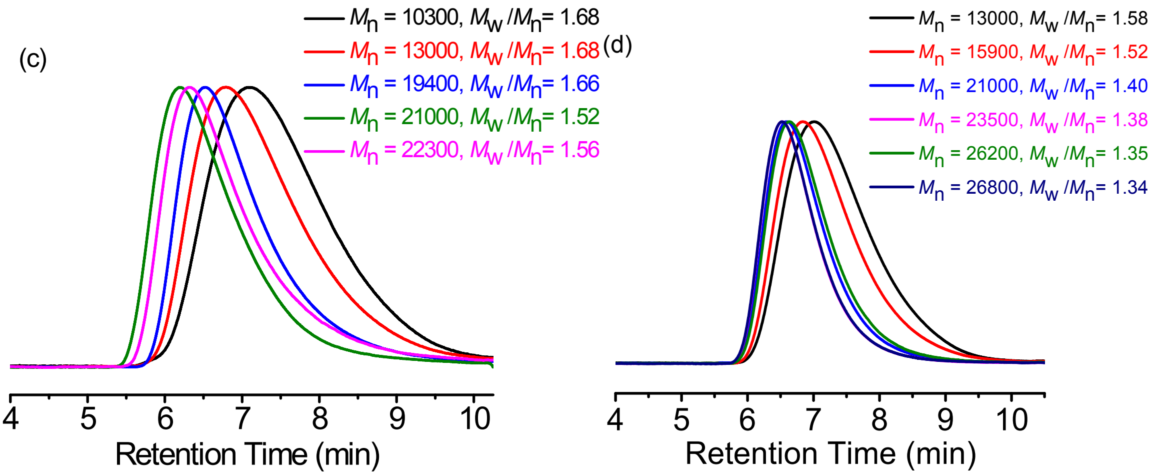


Figure S3. Polymerization behavior of blue light-induced RAFT copolymerization of MI(M1) and VAc(M2) at 25 °C using HFIP as solvent. (a) Relationships of *M*n and *M*w/*M*n with conversion in molar ratio of $[VAc]_0$ /$[MI]_0$ /$[EXEP]_0$ equals to 200/(200, 300, 133)/1; b-d) GPC traces of polymers obtained with molar ratio of $[VAC]_0$ /$[MI]_0$ equals to 200/200 (b), 200/300(c), 300/200(d).The unit of all the molecular weight showing in the GPC traces is g·mol^{-1}.

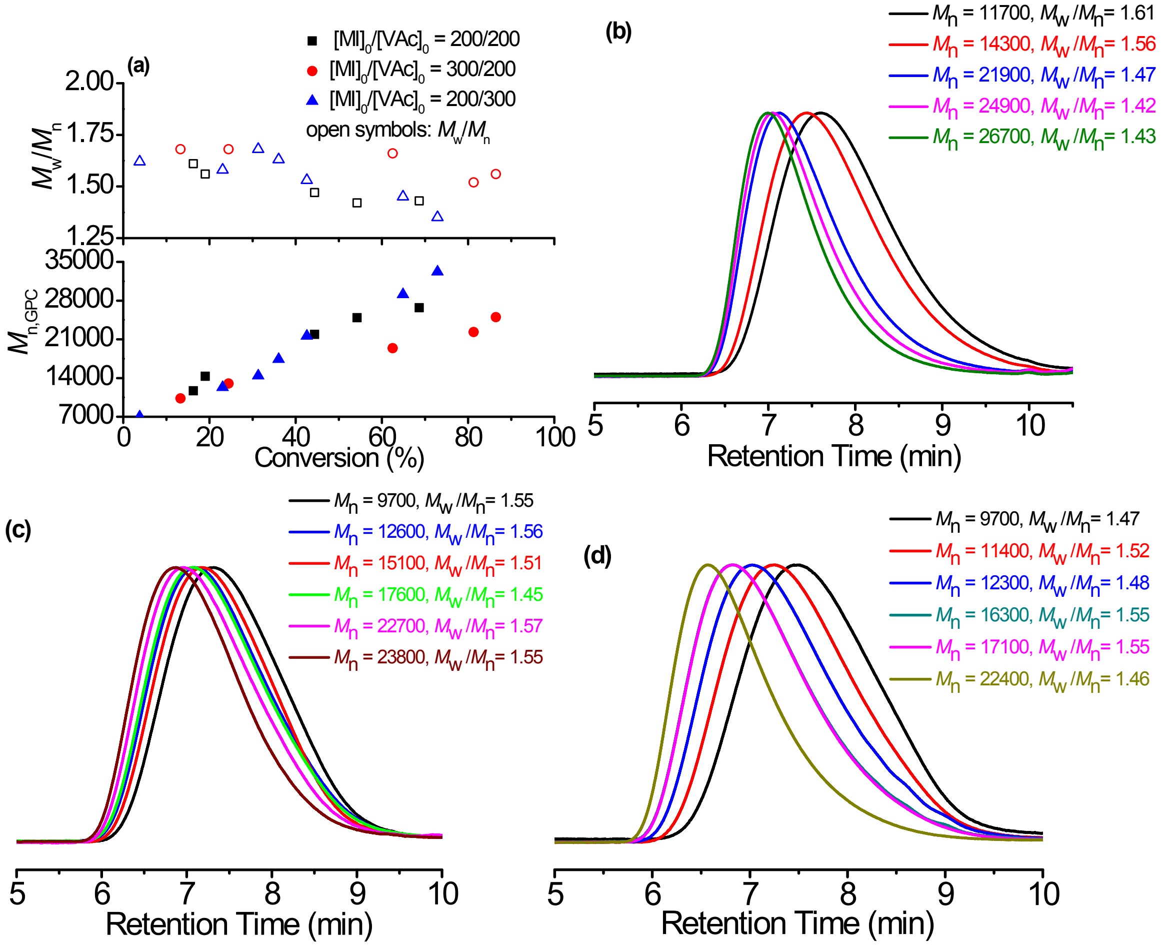


Figure S4. (a) Number-average molecular weights (*M*n) and molecular weight distributions (*M*w/*M*n) of the copolymers from blue light-induced and Xanthate (EXEP)mediated RAFT copolymerization of MI (M) and VAc (V) at 25 °C using Dioxane as solvent. $[VAC]_0$ /$[MI]_0$/$[EXEP]_0$ = 200/(200, 300, 133)/1. GPC traces: $[VAC]_0$/$[MI]_0$ = (b) 200/200, (c) 200/300, (d) 300/200. The unit of all the molecular weight showing in the GPC traces is g·mol^{-1}. Reaction conditions are the same as FigureS3.

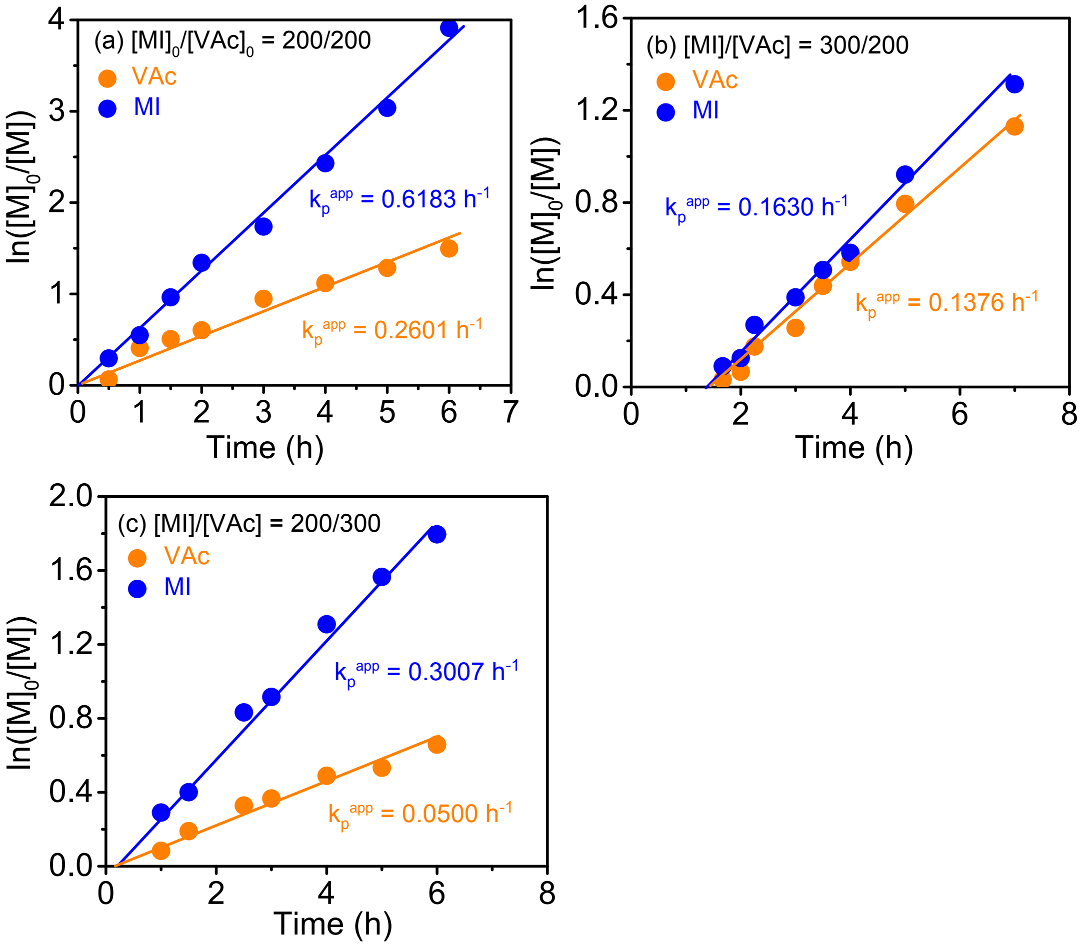
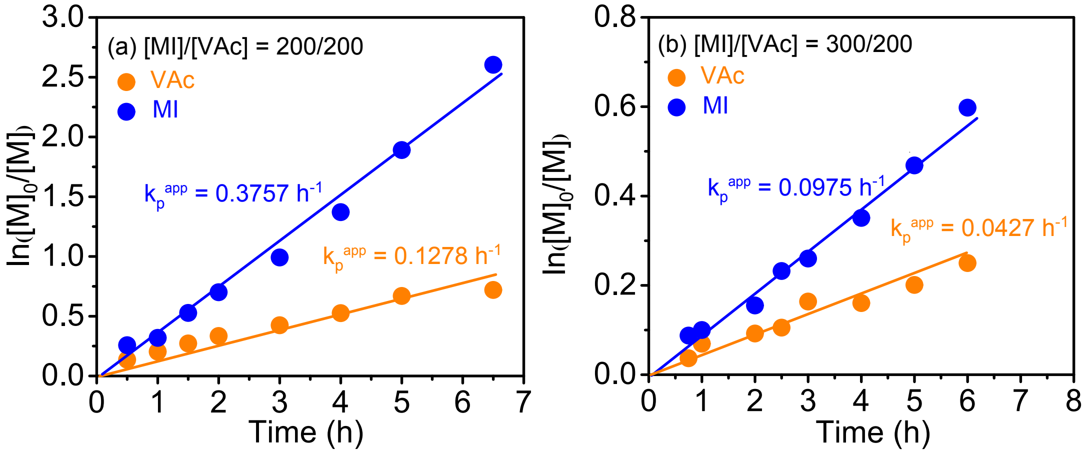


Figure S5. First-order kinetic plots for RAFT copolymerization of MI and VAc at 60 °C using HFIP as solvent. Different feeding ratio toward each graph: (a): $[VAc]_0$ /$[MI]_0$/$[EXEP]_0$/$[AIBN]_0$= 200/200/1/1; (b): $[VAc]_0$/$[MI]_0$/$[EXEP]_0$/$[AIBN]_0$= 200/300/1/1; (c): $[VAc]_0$/$[MI]_0$/$[EXEP]_0$/$[AIBN]_0$= 300/200/1/1



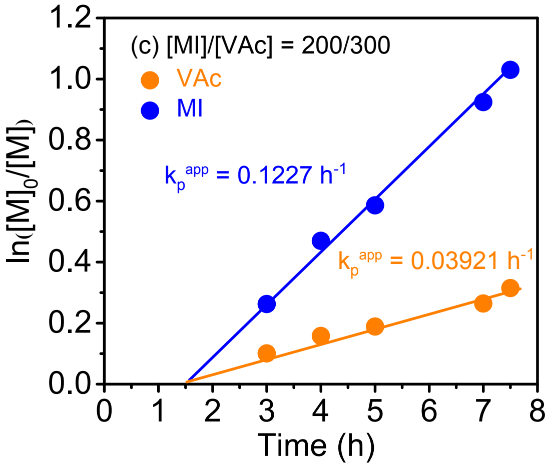


Figure S6. First-order kinetic plots for RAFT copolymerization of MI and VAc at 60 ºC using dioxane as solvent. Different feeding ratio toward each graph: (a): $[VAc]_0$ /$[MI]_0$/$[EXEP]_0$/$[AIBN]_0$= 200/200/1/1; (b): $[VAc]_0$/$[MI]_0$/$[EXEP]_0$/$[AIBN]_0$= 200/300/1/1; (c): $[VAc]_0$/$[MI]_0$/$[EXEP]_0$/$[AIBN]_0$= 300/200/1/1

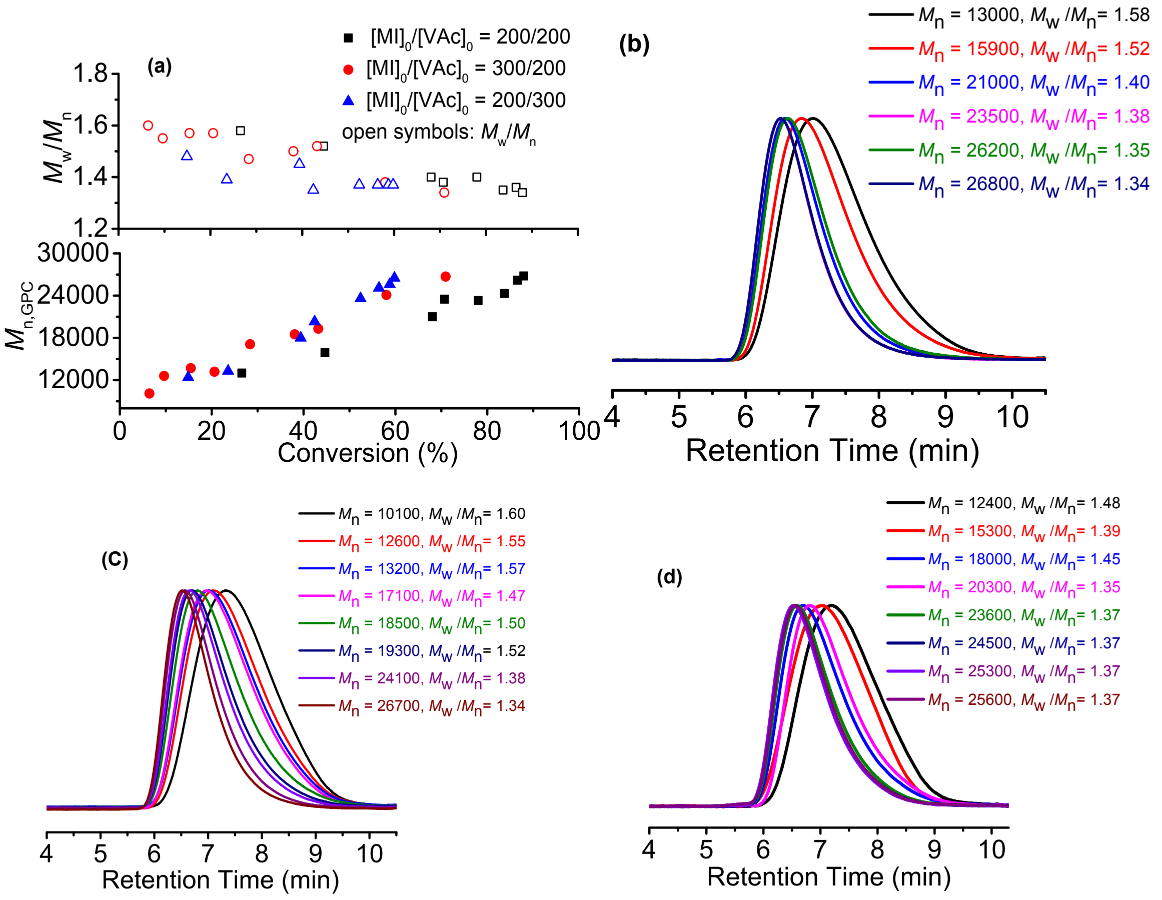


Figure S7. (a) Number-average molecular weights (*M*n) and molecular weight distributions (*M*w/*M*n) of the copolymers from thermal-induced and Xanthate (EXEP)mediated RAFT copolymerization of MI (M) and VAc (V) at 60 ºC using HFIP as solvent. $[VAC]_0$/$[MI]_0$/$[EXEP]_0$ = 200/(200, 300, 133)/1. GPC traces: $[VAC]_0$/$[MI]_0$ = (b) 200/200, (c) 200/300, (d) 300/200. The unit of all the molecular weight showing in the GPC traces gragh is g·mol^{-1}. Reaction conditions are the same as Figure S5.

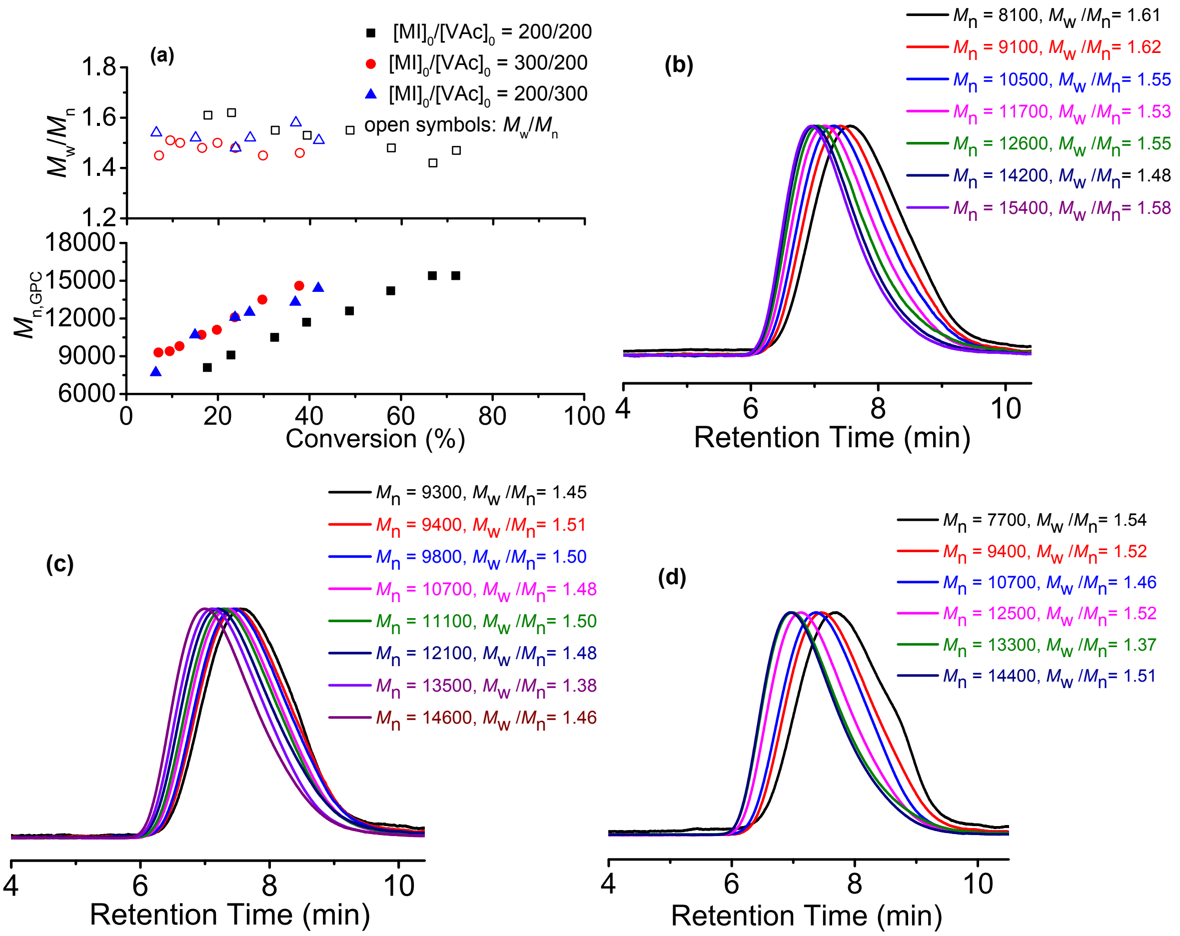


Figure S8. (a) Number-average molecular weights (*M*n) and molecular weight distributions (*M*w/*M*n) of the copolymers thermal-induced and Xanthate (EXEP) mediated RAFT copolymerization of MI (M) and VAc (V) at 60 ºC respectively using Dioxane as solvent. $[VAc]_0/[MI]_0/[EXEP]_0/[AIBN]_0$ = 200/(200, 300, 133)/1/1. GPC traces: $[VAc]_0/[MI]_0$ = (b) 200/20, (c) 200/300, (d) 300/200. Reaction conditions are the same as in Figure S7.

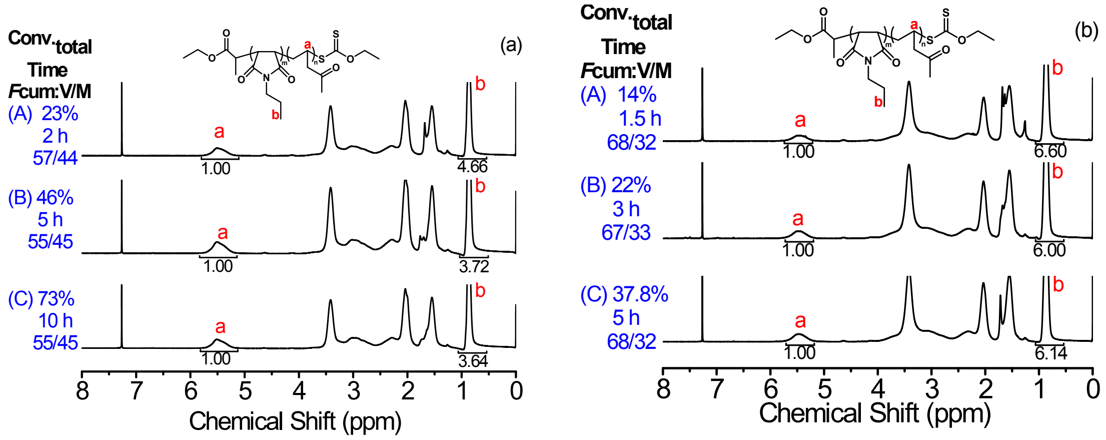


Figure S9. ^{1}H NMR spectra of the samples obtained from blue light-induced RAFT copolymerization of MI (M) and VAc (V) at 25 ºC respectively in HFIP (a) and in Dioxane (b). The feeding ratio of the copolymerization: $[VAc]_0/[MI]_0$ = 300/200. Reaction conditions are the same as in Figure S3.

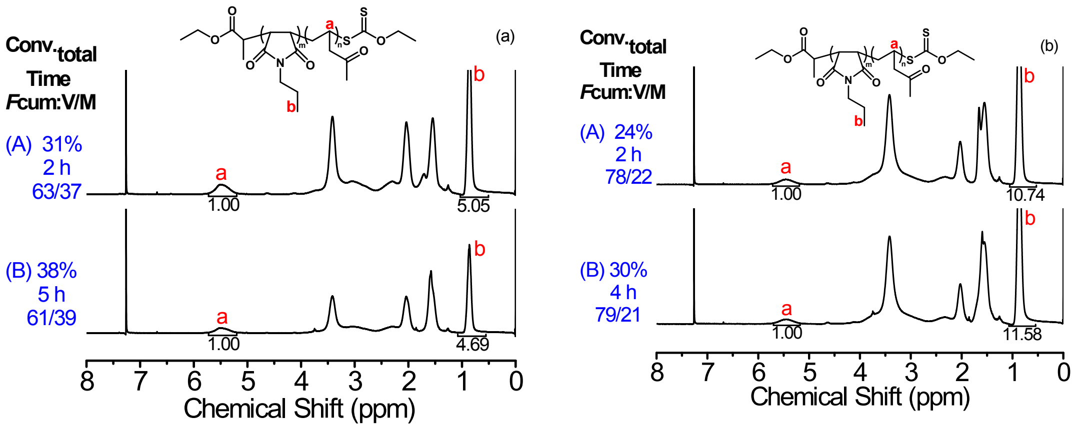


Figure S10. ^{1}H NMR spectra of the samples obtained from blue light-induced RAFT copolymerization of MI (M) and VAc (V) at 25 °C respectively in HFIP (a) and in Dioxane (b). The feeding ratio of the copolymerization: $[VAC]_0/[MI]_0 = 200/300$.

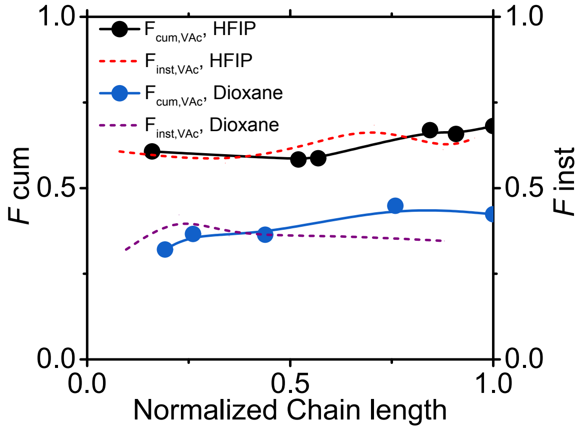


Figure S11. Cumulative (F_{cum}) or instantaneous (F_{inst}) monomer contents of VAc in copolymers as a function of normalized chain length. The calculation formulas of F_{cum}, F_{inst} and normalized chain length are demonstrated in Eqn. S1. All the products were obtained from RAFT copolymerization of MI (M) and VAc (V) at 25 °C respectively using HFIP or 1, 4-dioxane as solvent. Feeding ratio is $[VAC]_0/[MI]_0/[EXEP]_0 = 600/200/2$

Table S1. Data for the comparison with cumulative monomer contents of VAc in copolymers calculated from Elemental analysis ($Fcum_{(EA)}$) and ^{1}H NMR ($Fcum_{(conv.)}$) with different molecular weight.

Entry	solvent	$M_{n,GPC}$	$Fcum_{(conv.)}$		$Fcum_{(EA)}$	
			MI%	VAc %	MI%	VAc%
1[a]	HFIP	33200	49.6	50.4	50.0	50.0
2[a]	HFIP	19700	54.3	45.7	48.9	51.1
3[a]	Dioxane	11400	70.3	29.7	64.5	35.5

4^a	Dioxane	13300	72.7	27.3	68.2	31.8

a: All the copolymers were obtained from blue light-induced RAFT copolymerization of MI (M) and VAc (V) at 25 °C respectively in HFIP and in Dioxane. $[VAC]_0/[MI]_0/[EXEP]_0$ = 300/200/1/

Table S2. Data for calculating reactivity ratios of poly(MI-co-VAc) with HFIP as solvent.^{a}

$[MI]_0/[VAc]_0$	Con.$_{MI}$	Con.$_{VAc}$	M_{MI}	M_{VAc}	m_{MI}	m_{VAc}	F	*f*	*f*/F^2	(*f*-1)/F
20/80	0.163	0.119	0.200	0.800	0.256	0.745	0.250	0.342	5.479	-2.630
30/70	0.085	0.069	0.300	0.700	0.346	0.654	0.429	0.523	2.874	-1.101
50/50	0.079	0.068	0.500	0.500	0.537	0.463	1.000	1.162	1.162	0.162
60/40	0.157	0.119	0.600	0.400	0.664	0.336	1.500	1.979	0.880	0.653
70/30	0.062	0.068	0.700	0.300	0.679	0.320	2.333	2.120	0.389	0.480
80/20	0.167	0.129	0.800	0.200	0.838	0.162	4.000	5.178	0.324	1.045

a Copolymers obtained from different monomer feed compositions($[MI]_0/[VAc]_0$ = 20/200, 50/200, 100/20, 200/200, 200/50). m_{MI} and m_{VAc} refer to the MI and VAc composition in the copolymer, respectively. M_{MI} and M_{VAc} refer to the feed compositions of MI and VAc monomer, respectively. $f = m_{MI}/m_{VAc}$, $F = M_{MI}/M_{VAc}$. Reaction conditions are the same as Figure S3

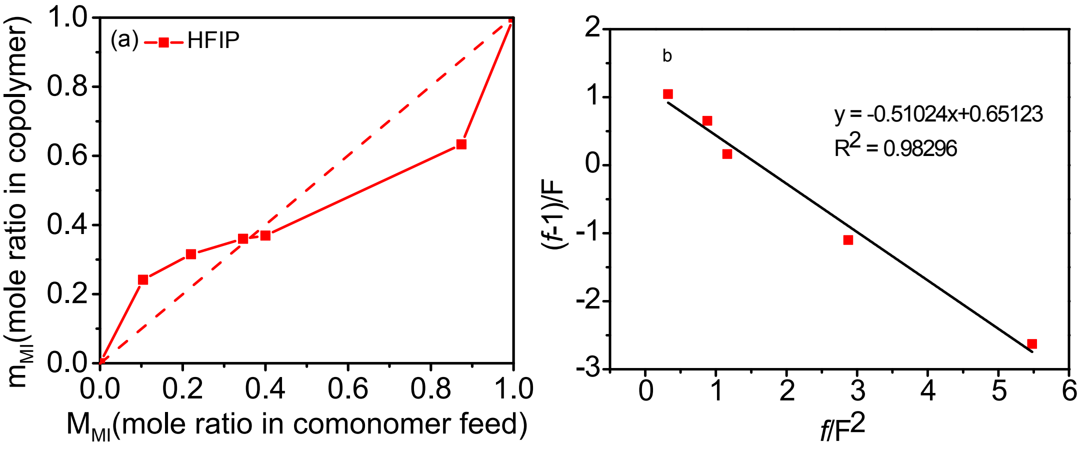


Figure S12. (a) Copolymer composition (m) as a function of the molar fraction of MI in the initial feed (M), and (b) plot of (f-1)/F Vs. f/F^2 for MI (M) and VAc (V) copolymerization with least-squares straight line in RAFT copolymerization at 25 °C with HFIP as solvent.

Table S3. Data for calculating reactivity ratios of poly(MI-co-VAc) with Dioxane as solvent.^{a}

$[MI]_0/[VAc]_0$	Conv. MI	Conv. VAc	M_{MI}	M_{VAc}	m_{MI}	m_{VAc}	F	*f*	*f*/F^2	(*f*-1)/F

50/200	0.035	0.022	0.193	0.807	0.796	0.204	0.239	3.894	68.077	17.100
100/200	0.029	0.017	0.341	0.659	0.801	0.199	0.517	4.025	15.032	5.846
300/200	0.065	0.074	0.600	0.400	0.748	0.252	1.500	2.963	1.317	1.308
200/100	0.107	0.093	0.661	0.339	0.851	0.149	1.950	5.703	1.500	1.812
200/50	0.080	0.085	0.800	0.200	0.830	0.170	4.000	4.883	0.305	0.971
200/20	0.092	0.078	0.966	0.034	0.902	0.098	28.412	9.246	0.011	0.290

a Copolymers obtained from different monomer feed compositions ($[MI]_0$ /$[VAc]_0$ = 50/200, 100/200, 300/200, 200/100, 200/50, 200/20). m_{MI} and m_{VAc} refer to the MI and VAc composition in the copolymer, respectively. M_{MI} and M_{VAc} refer to the feed compositions of MI and VAc monomer, respectively. f = m_{MI}/m_{VAc} , F = M_{MI}/M_{VAc}.

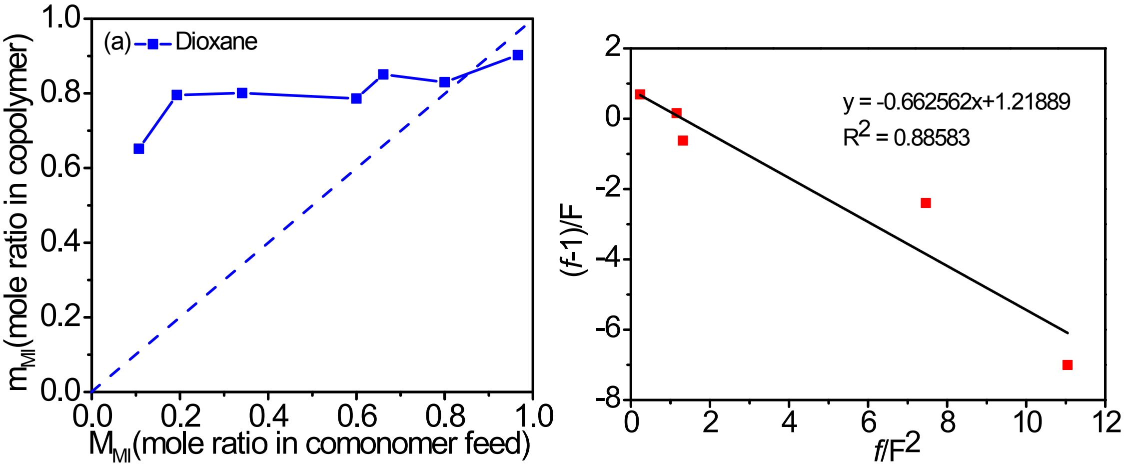


Figure S13. (a) Copolymer composition (m) as a function of the molar fraction of MI in the initial feed (M), and (b) plot of (f-1)/F Vs. f/F^2 for MI (M) and VAc (V) copolymerization with least-squares straight line in RAFT copolymerization at 25 °C with Dioxane as solvent.

Table S4. Data for calculating reactivity ratios of poly(MI-co-VAc) with HFIP as solvent at 60°C.[a]

[MI]$_0$ /[VAc]$_0$	Con.$_{MI}$	Con.$_{VAc}$	**M_{MI}**	**M_{VAc}**	**m_{MI}**	**m_{VAc}**	**F**	***f***	***f*/F^2**	**(*f*-1)/F**
20/80	0.054	0.055	0.200	0.800	0.197	0.803	0.250	0.245	3.927	-3.018
30/70	0.041	0.041	0.300	0.700	0.300	0.7.00	0.429	0.429	2.333	-1.333
40/60	0.062	0.052	0.400	0.600	0.443	0.557	0.667	0.795	1.788	-0.308
50/50	0.064	0.075	0.500	0.500	0.460	0.540	1.000	0.853	0.853	-0.147
60/40	0.053	0.068	0.600	0.400	0.539	0.461	1.500	1.169	0.520	0.113
70/30	0.078	0.073	0.719	0.281	0.714	0.286	2.540	2.493	0.386	0.588

a Copolymers obtained from different monomer feed compositions([MI]$_0$ /[VAc]$_0$ = 20/80, 30/70, 40/60, 50/50, 60/40, 70/30).

m_{MI} and m_{VAc} refer to the MI and VAc composition in the copolymer, respectively. M_{MI} and M_{VAc} refer to the feed compositions of MI and VAc monomer, respectively. f = m_{MI}/m_{VAc} , F = M_{MI}/M_{VAc}.

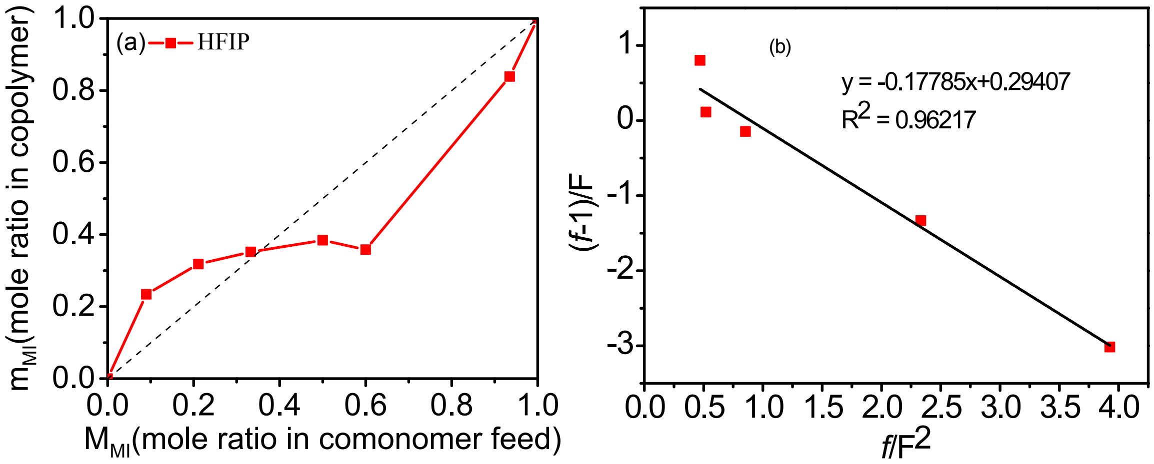


Figure S14. (a) Copolymer composition (m) as a function of the molar fraction of MI in the initial feed (M), and (b) plot of (f-1)/F Vs. f/F^2 for MI (M1) and VAc (M2) copolymerization with least-squares straight line in RAFT copolymerization at 60 °C with HFIP as solvent.

Table S5. Data for calculating reactivity ratios of poly(MI-co-VAc) with Dioxane as solvent at 60°C.[a]

[MI]$_0$ /[VAc]$_0$	**Con.$_{MI}$**	**Con.$_{VAc}$**	**M_{MI}**	**M_{VAc}**	**m_{MI}**	**m_{VAc}**	**F**	***f***	***f*/F^2**	**(*f*-1)/F**
100/200	0.162	0.024	0.333	0.667	0.302	0.698	0.252	0.433	6.813	-2.251
200/300	0.066	0.062	0.400	0.600	0.416	0.584	0.667	0.713	1.603	-0.430
300/200	0.036	0.093	0.600	0.400	0.367	0.633	1.500	0.580	0.258	-0.280
200/50	0.013	0.047	0.828	0.173	0.524	0.476	4.700	1.101	0.401	0.025
200/20	0.022	0.080	0.909	0.091	0.733	0.267	10.000	2.740	0.027	0.174

a Copolymers obtained from different monomer feed compositions ([MI]$_0$ /[VAc]$_0$ = 100/200, 200/300, 300/200, 200/20). m_{MI} and m_{VAc} refer to the MI and VAc composition in the copolymer, respectively. M_{MI} and M_{VAc} refer to the feed compositions of MI and VAc monomer, respectively. f = m_{MI}/m_{VAc} , F = M_{MI}/M_{VAc}.

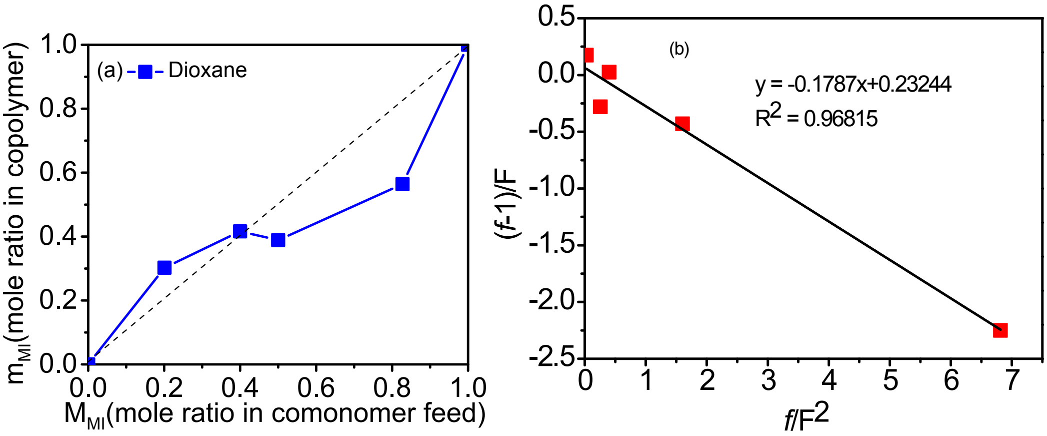


Figure S15. (a) Copolymer composition (m) as a function of the molar fraction of MI in the initial feed (M), and (b) plot of (f-1)/F Vs. f/F^2 for MI (M) and VAc (V) copolymerization with least-squares straight line in RAFT copolymerization at 60 °C with Dioxane as solvent. Reaction conditions are the same as Table S5.

Table S6. Data for calculating reactivity ratios of poly(MI-co-VAc) with HFIP as solvent.

[MI]$_0$/[VAc]$_0$	**Con.$_{MI}$**	**Con.$_{VAc}$**	**M$_{MI}$**	**M$_{VAc}$**	**m$_{MI}$**	**m$_{VAc}$**	**F**	***f***	***f*/F^2**	**(*f*-1)/F**
20/200	0.157	0.026	0.091	0.909	0.376	0.623	0.100	0.603	60.300	-3.970
50/200	0.173	0.085	0.200	0.800	0.338	0.662	0.250	0.511	8.192	-1.956
100/200	0.079	0.061	0.333	0.667	0.395	0.605	0.500	0.653	2.612	-0.694
200/200	0.128	0.125	0.500	0.500	0.505	0.495	1.000	1.020	1.020	0.02
200/50	0.026	0.059	0.800	0.200	0.636	0.364	4.000	1.747	0.109	0.186

Copolymers obtained from different monomer feed compositions([MI]$_0$ /[VAc]$_0$ = 20/200, 50/200, 100/200, 200/200, 200/50).

m$_{MI}$ and m$_{VAc}$ refer to the MI and VAc composition in the copolymer, respectively. M$_{MI}$ and M$_{VAc}$ refer to the feed compositions of MI and VAc monomer, respectively. f = m$_{MI}$/m$_{VAc}$, F = M$_{MI}$/M$_{VAc}$. Radical copolymerization of MI and VAc at 60 °C with HFIP as solvent and using AIBN as initiator.

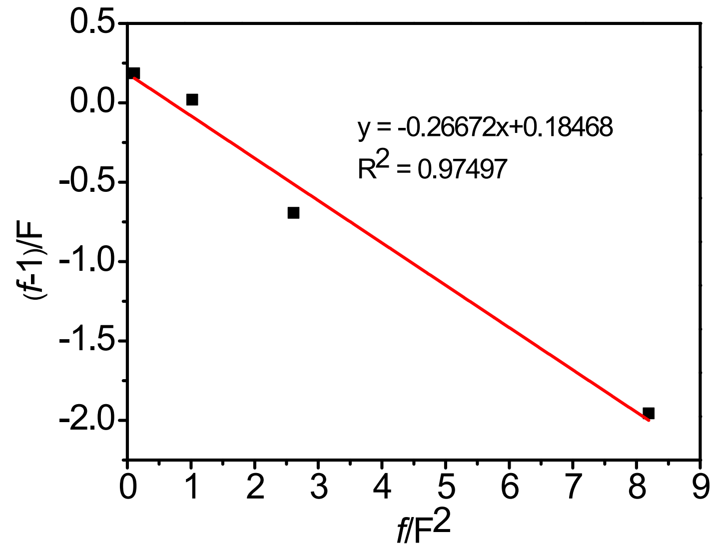


Figure S16. Plot of (f-1)/F Vs. f/F^2 for MI and VAc copolymerization with least-squares straight line in radical copolymerization at 60 ^{o}C with HFIP as solvent. $[MI]_0$ /$[VAc]_0$ = 50/200, 100/20, 200/200, 300/200, 200/20.

Table S7. Data for calculating reactivity ratios of poly(MI-co-VAc) with Dioxane as solvent.

$[MI]_0/[VAc]_0$	**Con.$_{MI}$**	**Con.$_{VAc}$**	**M_{MI}**	**M_{VAc}**	**m_{MI}**	**m_{VAc}**	**F**	***f***	***f*/F^2**	**(*f*-1)/F**
20/80	0.131	0.052	0.200	0.800	0.384	0.615	0.250	0.624	9.984	-1.504
40/60	0.225	0.172	0.366	0.634	0.430	0.570	0.667	0.755	1.697	-0.367
50/50	0.142	0.149	0.500	0.500	0.488	0.512	1.000	0.953	0.953	-0.047
70/30	0.020	0.035	0.700	0.300	0.571	0.429	2.333	1.333	0.246	0.143
80/20	0.031	0.062	0.800	0.200	0.667	0.333	4.000	2.000	0.125	0.250
90/10	0.044	0.051	0.900	0.100	0.886	0.114	9.000	7.765	0.096	0.751

Copolymers obtained from different monomer feed compositions ($[MI]_0$ /$[VAc]_0$ = 20/80, 40/60, 50/50, 70/30, 80/20, 90/10). m_{MI} and m_{VAc} refer to the MI and VAc composition in the copolymer, respectively. M_{MI} and M_{VAc} refer to the feed compositions of MI and VAc monomer, respectively. $f = m_{MI}/m_{VAc}$, $F = M_{MI}/M_{VAc}$.

Radical copolymerization of MI and VAc at 60 ^{o}C Radical copolymerization of MI and VAc at 60 ^{o}C with dioxane as solvent and using AIBN as initiator.

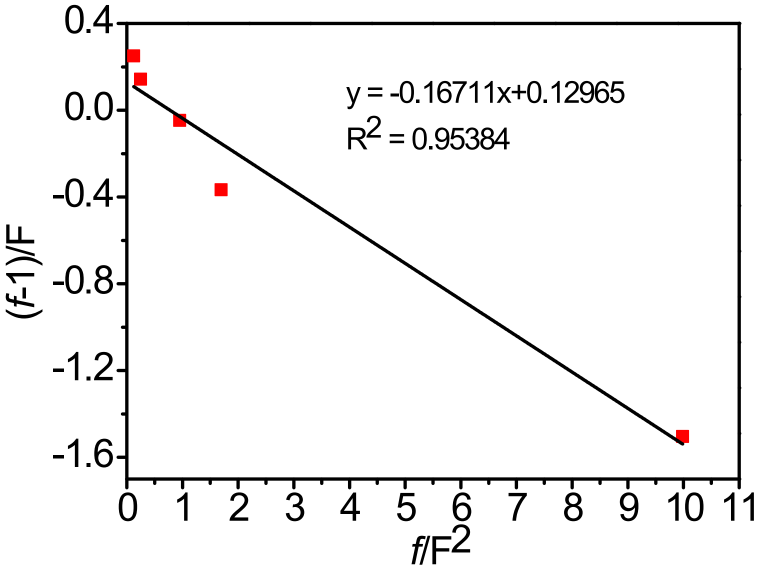


Figure S17. Plot of (f-1)/F Vs. f/F^2 for MI and VAc copolymerization with least-squares straight line in radical copolymerization at 60 ^{o}C with dioxane as solvent. [MI]$_0$ /[VAc]$_0$ = 20/80, 40/60, 50/50, 70/30, 80/20, 90/10

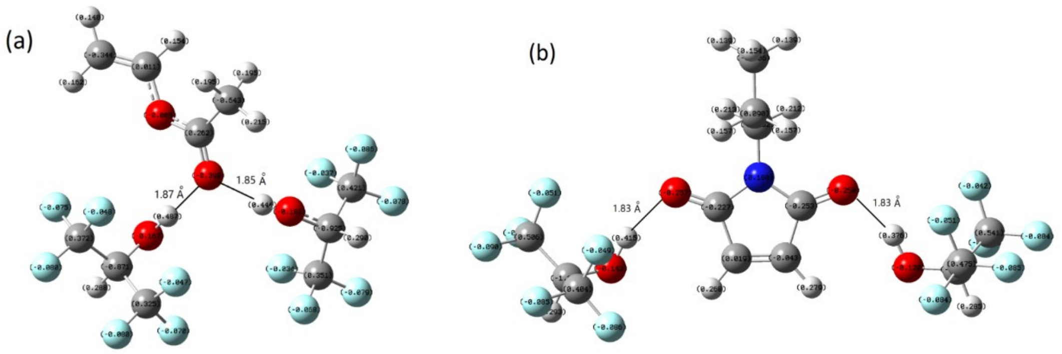


Figure S18. The Mulliken charges and the hydrogen bonding interaction of the VAc-HFIP (a) and MI-HFIP (b) at the level of B3LYP/6-311++G (d,p).

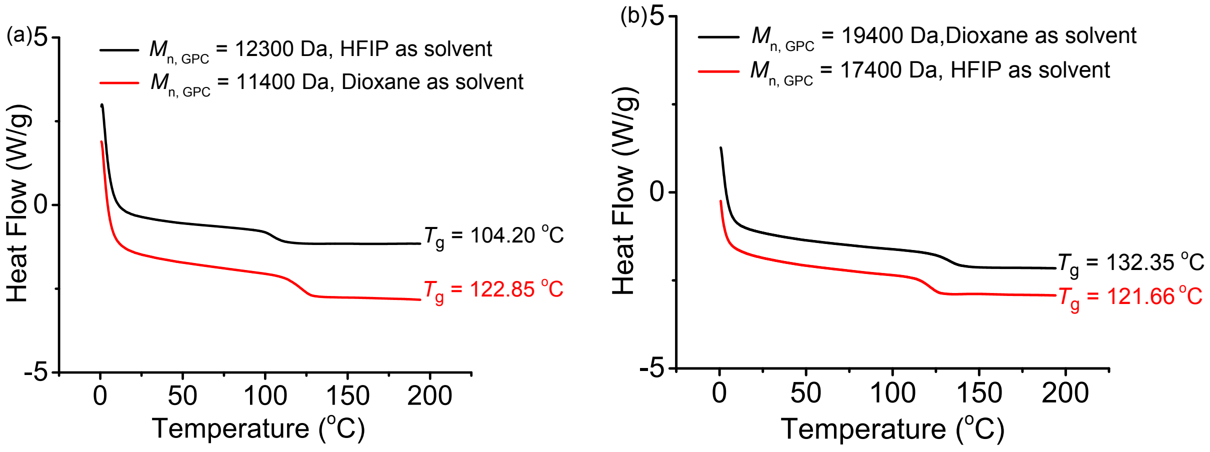


Figure S19. DSC thermograms of copolymers with different compositions (mol% of VAc and MI units) with HFIP and Dioxane as solvent, respectively, with a heating/cooling rate of 20°C/min from 0 to 200 °C under a continuous nitrogen flow.The feeding ratio of the copolymerization: (a) $[VAC]_0/[MI]_0$ = 300/200;(b) $[VAC]_0/[MI]_0$ = 200/300. Reaction conditions are the same as in Figure S3(b),(c).