Supporting information

The bulk RITP of MMA in the presence of HMPA with in situ formed alkyl iodide

Fig S1 shows the kinetic plot of ln([M]₀/[M]) versus time for the bulk polymerization of MMA with HMPA. It can be seen that the polymerization can be divided into two main stages, including inhibition period and polymerization period. The inhibition period is 6.5 h. The linearity of the kinetic plot in polymerization with HMPA in Fig S1 implies that the polymerizations are approximately first order with respect to the monomer concentration and the propagating radical concentrations remain constant through the polymerization process.



Fig. S1 Kinetic plots of $ln([M]_0/[M])$ versus time for the bulk polymerization of MMA with HMPA. [MMA]_0:[I_2]_0:[ABVN]_0:[HMPA]_0 = 200:1:1.6:1. Temperature = 60 °C. $M_{n,th} = M_{A-I} + 2[M]_0 / [I_2]_0 \times M_{MMA} \times$ conversion %.

Effect of solvents on polymerization of MMA with HMPA and in situ formed alkyl iodide

Fig S2 shows the kinetic plot of ln([M]₀/[M]) versus time for the bulk polymerization of MMA with HMPA in different solvents (anisole and toluene). It can be seen that the polymerization rate of anisole system is faster than that of toluene. The inhibition period is 2.05 h and 2.40 h for anisole and toluene, respectively. Good agreement between theoretical and experimental molecular weights was observed in all cases and PDI kept small (PDI<1.24) in the process of polymerization (Fig S3).



Fig. S2 Kinetic plots of $\ln([M]_0/[M])$ versus time for the solution polymerization of MMA with HMPA. [MMA]_0:[I_2]_0:[ABVN]_0:[HMPA]_0 = 200:1:1.7:2. Temperature = 65 °C. $M_{n,th} = M_{A-I} + 2[M]_0 / [I_2]_0 \times M_{MMA} \times$ conversion %.



Fig. S3 Number-average molecular weight and molecular weight distribution versus conversion. For conditions see those in Fig. S2

Preparation of 2-iodo-2-methylpropionitrile (CP-I) for different reaction time.

A solution of iodine (7.5 mM) and AIBN (24.3 mM) in toluene (10.5 g) was heated under an

argon atmosphere at 100 °C in a thermostated block heater in the absence of light. After the desired reaction time, the slightly yellowish reaction mixture was rapidly cooled to room temperature. The solution of CP-I in toluene was then used without purification. The composition of CP-I solution was determined by ¹H NMR in CDCl₃. The conversion of iodine to CP-I was about 99.5%. And the mass fraction of CP-I in toluene and residual rate of AIBN were determined with the method of ¹H NMR.

 $\frac{\text{ICP - I \times MCP - I}}{\text{Mass fraction of CP-I} = \frac{\text{ICP - I \times MCP - I} + \text{IToluene } + \text{ITMSN } \times \text{MTMSN}}{\text{Eqn. (S1)}}$

Entry	Time (min)	Mass fraction of CP-I (%)	Residual quantity of AIBN in CP-I solution(wt %)	[CP-I] ₀ :[AIBN] ₀ ^a
1	15	18.12	1.5	1:0.1
2	30	18.34	0.75	1:0.05
3	60	18.21	0	∞

Table S1 Preparation of 2-iodo-2-methylpropionitrile for different time.

^a residual AIBN.



Fig. S4 ¹H NMR spectra of the solution of iodine and AIBN in toluene after heated at 100 °C for 15 min.



Fig. S5 ¹H NMR spectra of the solution of iodine and AIBN in toluene after heated at 100 °C for 30 min.



Fig S6. ¹H NMR spectra of the solution of iodine and AIBN in toluene after heated at 100 °C for 60 min.

The polymerization of MMA with combination of alkyl iodide and HMPA

Fig S7 shows the number-average molecular weight and molecular weight distribution versus conversion for polymerization with residual AIBN in CP-I solution ($[CP-I]_0:[AIBN]_0=1:0.1$). The measured values of number-average molecular weight are close to their calculated values. Besides, molecular weight distributions are very low (PDI < 1.24).



Fig. S7 Number-average molecular weight and molecular weight distribution versus conversion. [MMA]₀:[CP-I]₀:[HMPA]₀:[AIBN]₀=100:1:1:0.1; $M_{n,th} = M_{A-I} + 2 [M]_0 / [I_2]_0 \times M_{MMA} \times \text{conversion }\%.$

Synthesis of tetramethylsuccinodinitrile (TMSN)

A solution of AIBN (4.000 g, 24.359 mM) in toluene (10.5 g) was heated under an argon atmosphere at 100 °C in a thermostated block heater. After full reaction, the transparent reaction mixture was rapidly cooled to room temperature. The composition of the obtained solution was determined by ¹H NMR in CDCl₃, demonstrating no residual AIBN. And then the product was concentrated to yield white crystals.



Fig. S8 ¹H NMR spectra of the solution of TMSN in toluene.

The solution polymerizations of MMA with in situ formed alkyl iodide and TMSN

In order to study the effects of TMSN on the polymerizations, we carried out a series of polymerizations with TMSN. (Table S2) The results indicated that the number-average molecular weight value didn't agree with its corresponding theoretical one, and the corresponding M_w/M_n values of polymerization with TMSN are very large. ($M_w/M_n > 1.45$). Thus, TMSN cannot control the polymerizations, which can be inferred that HMPA can well regulate the polymerization process rather than TMSN.

Entry	Azo Initiator	[MMA] ₀ /[I ₂] ₀ /[Azo] ₀ /[TMSN] ₀	T(°C)	Time(h)	Conv. (%)	$M_{\rm n,GPC}$ / $M_{\rm n,th}$ (g mol ⁻¹) ^a	PDI
1	ABVN	200:1:1.7:1.5	65	5.5	84.4	7200 / 8400	1.47
2	ABVN	200:1:1.7:2	65	7	80.3	9400 / 8000	1.45
3	AIBN	200:1:1.5:3	80	8	87.6	15000/8800	1.51

 Table S2 Polymerization of MMA with TMSN

^a $M_{n,th} = M_{A-I} + 2[M]_0 / [I_2]_0 \times M_{MMA} \times \text{conversion }\%.$

Reaction of CP-I, HMPA and TEMPO

A mixture of toluene(1.8mL), CP-I (1.5 mM), HMPA (1.5 mM), and TEMPO (1.5 mM) in a Schlenk flask was heated at different temperature for different time under argon atmosphere with magnetic stirring. After the desired reaction time, samples were withdrawn periodically under argon using a deoxygenated syringe, and analyzed by ¹H NMR in CDCl₃.



Fig. S9 ¹H NMR spectra of the solution of CP-I (1.5 mM), HMPA (1.5 mM), and TEMPO (1.5 mM) heated at 50 °C for 12 h and 60 °C for 8 h.

The preparation of high-molecular-weight polymers with narrow distribution

The tracts of the GPC data of the samples in Entry 4 (in Table 5) were shown in Fig. S10. The results showed that the polymer dispersion coefficient slightly increases with the monomer conversion.



Fig. S10 Typical GPC traces from the synthesis of PMMA samples in Entry 4 (in Table 5) by the polymerization with alkyl iodide initiator and HMPA.