Electronic Supplementary Information for

Mechanochemical production of phenyl cations
through heterolytic bond scission

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Figure S1. $^1$H NMR spectrum of compound 1; solvent: CDCl$_3$.

Figure S2. $^1$H NMR spectrum of TAS initiator; solvent: CDCl$_3$.
Figure S3. $^1$H NMR spectra of PMA-TAS ascribable to (a) TAS group and (b) PMA; solvent: CDCl$_3$.

Figure S4. CoGEF for model TAS at B3LYP 6-31G* level of theory.
Figure S5. GPC traces (RI) before (black) and after (red) sonication of PMA-TAS.

Figure S6. $^1$H NMR spectra of PMA-TAS (a) before and (b) after sonication and (c) after UV light irradiation; solvent: CDCl$_3$, sonication: 60 min in acetonitrile under a N$_2$ atmosphere at 6 °C, UV light irradiation: High-pressure Hg ramp, 4000 mW/cm$^2$, 15 min.
Figure S7. Comparison of $^1$H NMR spectrum of (a) TAS initiator itself with ones of sonicated TAS initiator (b) itself or (c) with homo PMA; solvent: CDCl$_3$, sonication: 60 min in acetonitrile under a N$_2$ atmosphere at 6 °C.

Figure S8. $^{19}$F NMR spectra of (a) sonicated TAS initiator with homo PMA and photo-activated TAS initiator (b) itself or (c) with homo PMA; solvent: CDCl$_3$, sonication: 60 min in acetonitrile under a N$_2$ atmosphere at 6 °C, UV light irradiation: High-pressure Hg ramp, 4000 mW/cm$^2$, 15 min.
Figure S9. GPC traces (RI) before (black solid line) and after (blue dot line) sonication of low molecular weight PMA-TAS (19 kDa).

Figure S10. $^{19}$F NMR spectra of low molecular weight PMA-TAS (19 kDa) before and after sonication: 60 min in acetonitrile under a N$_2$ atmosphere at 6 °C.
Figure S11. $^1$H spectra of low molecular weight PMA-TAS (19 kDa) before and after sonication: 60 min in acetonitrile under a $\text{N}_2$ atmosphere at 6 °C.

Figure S12. UV/vis absorption spectra of MAMA in THF. The spectrum was collected by the PDA detector equipped in the GPC system.
Figure S13. GPC analysis results for the mixture of PMA-TAS and MAMA without sonication; (a) RI and UV (378 nm) signals (black solid line and red dash line, respectively) and (b) absorption spectrum of the polymer component (retention time 26.4 min). UV absorption data were collected by the PDA detector equipped in the GPC system.