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Supplementary Information

Solvent-induced Competing Processes in Polycarbonate Degradation: Depolymerization, Chain Scission, and Branching/Crosslinking

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Additional Experiments and Methods.

Calculation of Flory-Huggins Interaction Parameter. The Flory-Huggins interaction parameter between PC and a solvent, $\chi_{PC-Solvent}$, was calculated according to the following equation:¹

$$\chi_{PC-Solvent} = \frac{V_m a}{RT} [(\delta_{PC,d} - \delta_{S,d})^2 + 0.25(\delta_{PC,p} - \delta_{S,p})^2 + 0.25(\delta_{PC,h} - \delta_{S,h})^2]$$

where V_m is the molar volume of the solvent; *a* is a constant with a recommended value of 0.6; $\delta_{PC,d}$, $\delta_{PC,p}$, and $\delta_{PC,h}$ are the dispersion, polarity, and hydrogen bonding component, respectively, of the Hansen solubility parameter of polycarbonate; $\delta_{S,d}$, $\delta_{S,p}$, and $\delta_{S,h}$ are the dispersion, polarity, and hydrogen bonding component, respectively, of the Hansen solubility parameters of the solvent. The parameters are summarized in Table S1. χ_{PC-DMF} is lower than $\chi_{PC-DMSO}$, suggesting that PC has a higher solubility in DMF than in DMSO.

Solubility Test of PC in DMSO and DMF. PC (50 mg) was added to DMSO (5 mL) and DMF (5 mL) at 50 °C under stirring of 300 rpm. PC was dissolved in DMF but only swollen in DMSO. A photograph (**Fig. S3**) was taken after 3 hours.

Collection of CO₂ of PC Degradation in DMF. In the GC chromatogram (**Fig. S8A**), the peak intensity of produced CO₂ from PC degradation was much stronger than the CO₂ in the atmospheric background. GC chromatograms showed about three times more feedback signals from PC degradation in DMF, indicating that the CO₂ signals collected are primarily from the reaction.

Solubility Test of X-PC and Pristine PC in DMF. The solubility test was performed by charging 20

mg of polymer powders (B/X-PC or pristine PC) into 2 mL of DMF. Pristine PC dissolved after 5

min while B/X-PC was not dissolved after 2 days. The photograph was taken after 2 days.

Additional Tables.

Table S1. Hansen solubility parameters ($\delta_{solvent}$), PC-solvent interaction parameter ($\chi_{PC-solvent}$), Hansen total solubility parameters (δ_t), and molar volume of solvents.

compound	Hansen solubility parameters			XPC-solvent	δ_t^c	V _m c
	$\delta_{i,d}$	δ _{i,p}	$\delta_{i,h}$		(IMPa ^{0.5})	(cm³)
PC (Lexan 144R) ^a	20.3	2.5	8.1	-	22.0	-
DMF	17.4	13.7	11.3	0.87	24.8	82.6
DMSO	18.4	16.4	10.2	0.91	18.6	71.2

^a Hansen solubility parameters of PC were found in the literature.²

 b The Flory-Huggins parameter $\chi_{\text{PC-solvent}}$ was calculated based on the Hansen solubility parameters (Eq. S1).¹

^c Hansen total solubility parameters ($\boldsymbol{\delta}_t$), and molar volume at standard conditions.

Table S2. Mass of pristine PC in the degradation reaction in DMSO.

	Mass of PC total	Mass of undissolved PC	Mass of dissolved PC	
	(Heterogeneous		(Homogenous	
	reaction)		reaction)	
Reaction #1	50.0 mg	37.9 mg	12.1 mg	
Reaction #2	50.2 mg	40.2 mg	10.0 mg	
Reaction #3	49.8 mg	38.6 mg	11.2 mg	
Average	50.0 mg	38.9 mg	11.1 mg	

Additional Figures.



Fig. S1 EDS spectrum of the synthesized CuS NPs. The atomic ratio of Cu to S is ~ 1:1 based on atomic percentage of Cu and S as detected by EDS (inset).



Fig. S2 Histogram of particle size distribution. The average diameter of 304.7 nm was based on 100 particles.



Fig. S3 Photograph of 50 mg of PC swollen in 5 mL of DMSO (left) and dissolved in DMF (right) after stirring for 3 h at 50 °C.



Fig. S4 GPC traces of PC degradation in DMF at 80 $^\circ C$ for 72 h and at 140 $^\circ C$ for 24 h without CuS NPs.



Fig. S5 (A) Full spectra and (B) magnified view of ¹³C-NMR of pristine PC, PC/CuS NPs in DMF, and PC/CuS NPs in DMSO. Peaks were assigned to the corresponding carbons in PC. ¹³C-NMR solvent was $CDCl_3$. PC and CuS NPs were added to DMF or DMSO and then stirred at room temperature for 1 d.



Fig. S6 (A) Magnified GC chromatogram and (B) MS spectra of degraded products after PC degradation in DMF.



Fig. S7 ¹H-NMR of DMF in CD_2Cl_2 with $CHCl_3$ as an internal reference. Integration over the proton peaks of $CHCl_3$, DMF, and water affords the calculation of the water percentage in DMF. About 3.7 wt. % water was determined in DMF.



Fig. S8 (A) Extracted-ion GC chromatogram of CO_2 produced from PC degradation in DMF at 80 °C. The background CO_2 in the air was subtracted. Ion extraction (m/z) was set at 44. (B) Photograph of the sealed reactor where this reaction was conducted.



Fig. S9 GPC traces of PC degradation in anhydrous DMF at 80 °C under N₂ purging.



Fig. S10 (A) GC chromatogram and (B) MS spectra of PC after the degradation reaction in anhydrous DMF at 80 °C for 72 h. Quantitative conversion analysis was shown in the inset. DPC, diphenyl carbonate. BPA, bisphenol-A.



Fig. S11 GPC traces (with THF as the mobile phase) of B/X-PC and pristine PC. The bimodal peak intensities of B/X-PC were taken for the quantitative analysis (inset). Since B/X-PC cannot be fully dissolved in DMF, GPC with THF as mobile phase was used to estimate the degree of dn

branching/crosslinking. The specific refractive index increment (\overline{dc}) of PC in in THF was determined to be 0.185 mL/g.



Fig. S12 GPC traces of (A) homogeneous degradation of PC in DMSO at 100 °C and (B) heterogeneous degradation of PC in DMSO at 50 °C. The PC in both reactions showed branching/crosslinking after 48 h.



Fig. S13 GPC traces of PC without CuS NPs: (A) homogeneous degradation in DMSO at 50 °C for 72 h and (B) heterogeneous reaction in DMSO at 100 °C for 30 h.



Fig. S14 GPC traces of PC degradation in DMSO with or without H_2O_2 under the conditions of (A) homogeneous reaction at 50 °C for 72 h and (B) heterogeneous reaction at 100 °C for 72 h. The GPC trace in black corresponds to the pristine PC. The concentration of H_2O_2 in the reaction was 100 mM.



Fig. S15 Kinetic fittings of the degree of polymerization (DP) as a function of PC degradation time into chain-end scission mechanism: (A) in DMF at 80 °C (blue) and 140 °C (brown) and (B) homogeneously in DMSO at 50 °C. Fitting equations and R-values were included.



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Fig. S16 ¹³C-NMR of B/X-PC (after heterogeneous reaction at 100 °C in DMSO), PC oligomer (after homogeneous reaction at 50 °C in DMSO), and pristine PC dissolved in CDCl₃. Peaks were assigned to corresponding carbons in the PC backbone.



Fig. S17 DSC thermograms of pristine PC and B/X-PC. Scan rate: 10 °C/min. After each heating, the samples were subject to 5-min isothermals to ensure that the samples were stabilized thermally.



Fig. S18 Reaction scheme (A) and GPC traces (B) of PEI degradation in DMSO.

References

1. C. M. Hansen, *Hansen Solubility Parameters: A User's Handbook, 2nd edition*. Boca Raton, FL, 2007.

2. C. K. Kjellander, T. B. Nielsen, A. Ghanbari-Siahkali, P. Kingshott, C. M. Hansen, K. Almdal, *Polym. Eng. Sci.*, 2008, **93**, 1486-1495.