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How to accelerate thermal poly(propylene carbonate) degradation?

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Experimental part

Degradation experiments

In polymerization – degradation experiments, polymerizate was subjected to thermal treatment directly without quenching catalyst.

In other degradation experiments, the catalyst was quenched with HCl. The polymer was purified thoroughly by repeating of three cycles of precipitation – filtration – dissolution – precipitation. The amount of residual catalyst was analyzed by ICP-MS. Aiming this, about 100 mg of PPC was subjected to ashing at 550 ^{o}C during 3 h; the residue was diluted in the concentrated HCl solution (10 ml) and the elemental composition of the resulting mixture was investigated.

In experiments with salen complexes of Co^{II} and Co^{III}, the desired amount of salen complex (10^{-3} mol dm^{-3}) was dissolved in 1 ml of NMP or DMF and the solution was added to 50 mg of a polycarbonate. Other concentrations of salen complexes were prepared by dilution of the initial solution. In experiment with AIBN, a solution containing 10^{-1} mol dm^{-3} of AIBN and 50 mg of a polycarbonate in 1 ml of 1,4-dioxane was prepared. In experiment with cumyl hydroperoxide, initiator and a polymer were weighed and dissolved in 1 ml of hot (~50 °C) ethylene carbonate.

All the prepared solutions were poured into ampoules, degassed, and the ampoules were sealed. The ampoules were put into oil bath preheated to desired temperature. After that, the ampoules were cooled by placing into iced water and the reaction mixture was analyzed by NMR and SEC. The typical ^{1}H NMR spectra are given below. In the spectra, signals at 4.98, 4.11 - 4.28 and 1.26 ppm are attributed to polycarbonate, while signals at 4.79 - 4.92, 4.46 - 4.50, and 3.95 - 3.99 ppm are attributed to propylene carbonate.

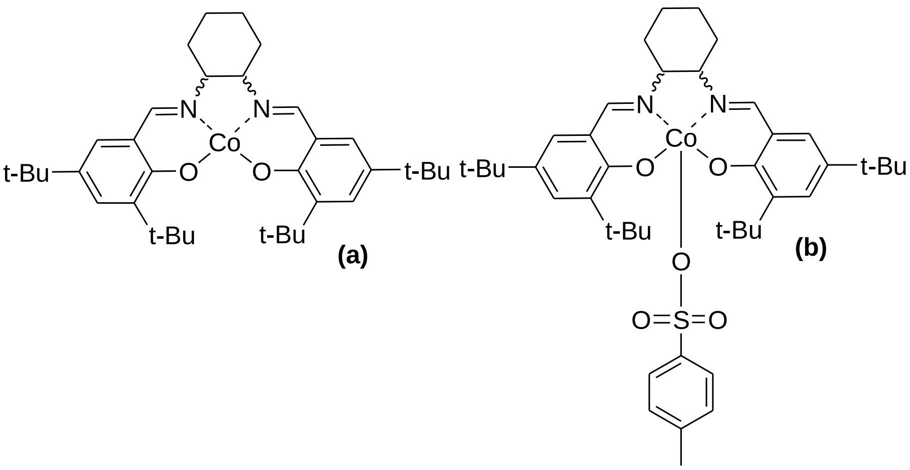
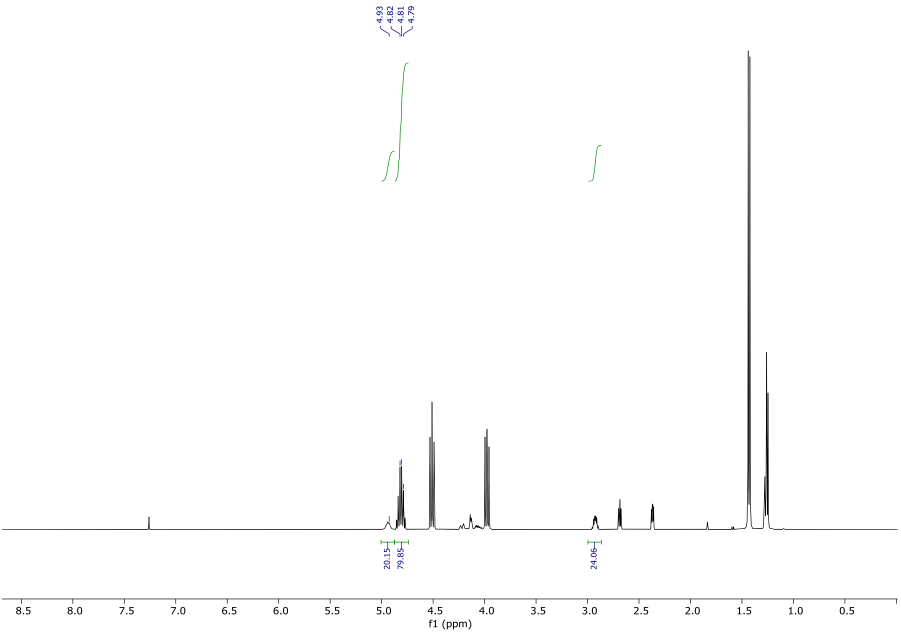
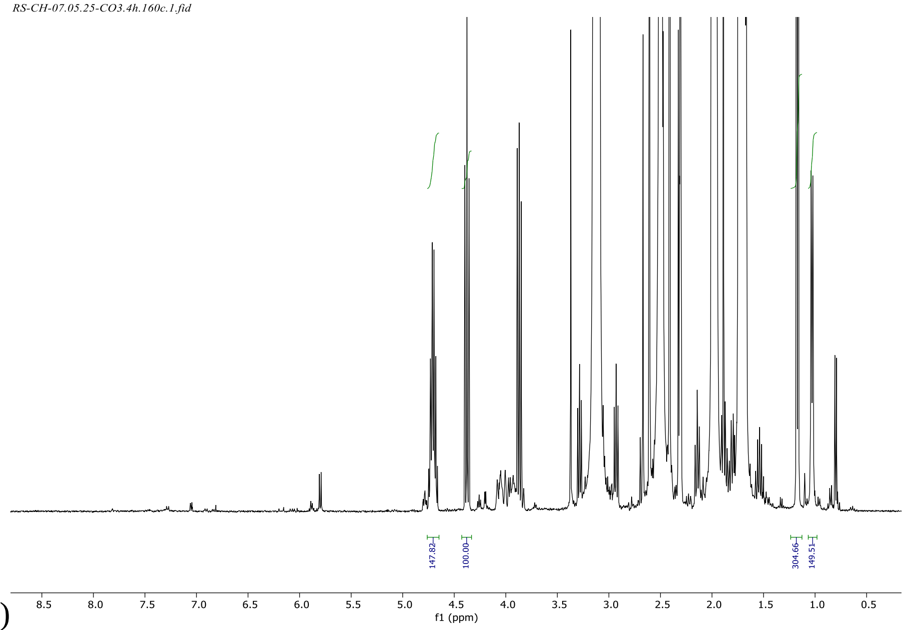


Figure S1. Chemical structures of salen complexes Co^{II} (a) and Co^{III} (b)



(a)



(b)

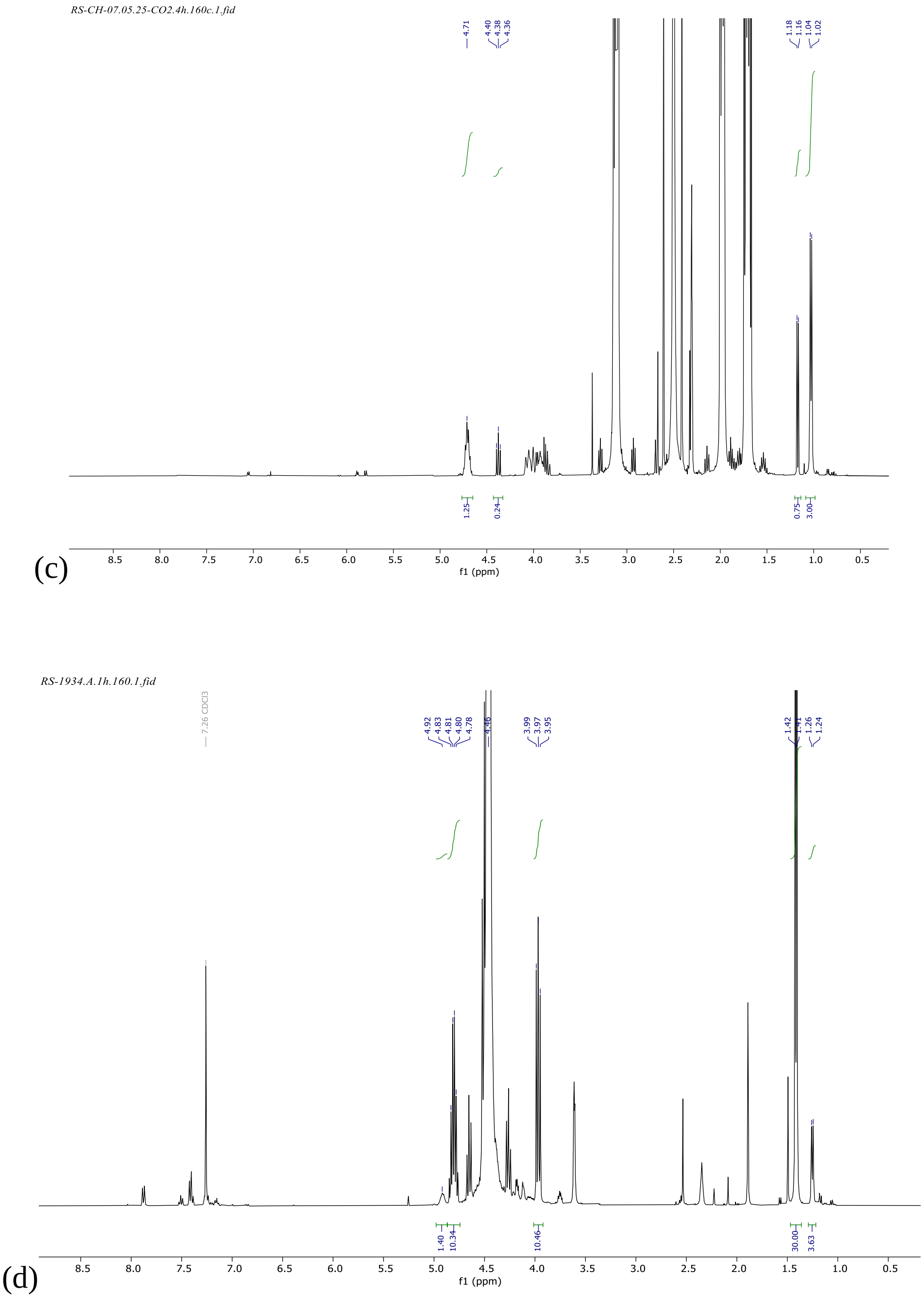


Figure S2. ^{1}H NMR spectra ($CDCl_3$) of polycarbonate subjected to degradation: (a) polymerization – depolymerization experiment after heating at 130°C for 40 min; (b) heating PPC solution in NMP in the presence of Co^{II} at 160°C for 4 h; (c) heating PPC solution in NMP in the presence of Co^{III} at 160°C for 4 h; (d) heating PPC solution in ethylene carbonate in the presence of cumene hydroperoxide at 160°C for 1 h.

Methods

NMR spectra were obtained on a Bruker Avance III HD (400 MHz ^{1}H) in $CDCl_3$. The SEC measurements were performed in THF at 40 °C with a flow rate of 1.0 ml min^{-1} using a 1260 Infinity II GPC/SEC Multidetector System chromatograph (Agilent, Santa Clara, CA, USA) equipped with two PLgel 5 μm MIXED B columns. The SEC system was calibrated using narrow dispersed linear poly(methyl methacrylate) standards with MW ranging from 0.8 to 2000 kDa.

Ashing was carried out using muffle furnace P330 (Nabertherm) followed by the study of elemental composition of the resulting mixture by ICP-MS. ICP-MS was carried out on an Elan DRC-e device (Perkin-Elmer) with the following parameters: operating frequency of the ICP generator 40 MHz; output power 1.1 kW; plasma-forming argon flow 15 dm^3 min^{-1}; argon transport flow 0.90 dm^3 min^{-1}; argon cooling flow 0.5 dm^3 min^{-1}; sample flow rate 0.85 ml min^{-1}.

Polymerization – degradation experiments

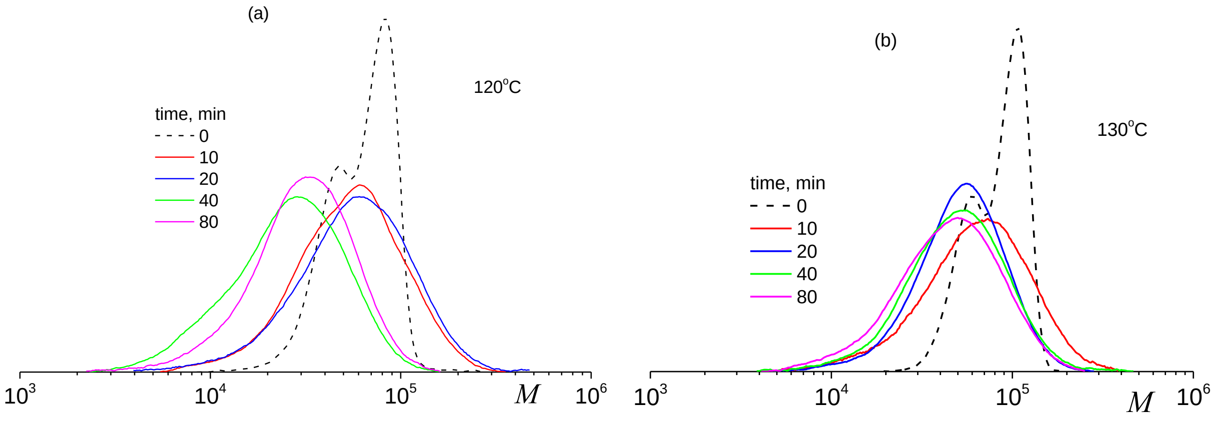
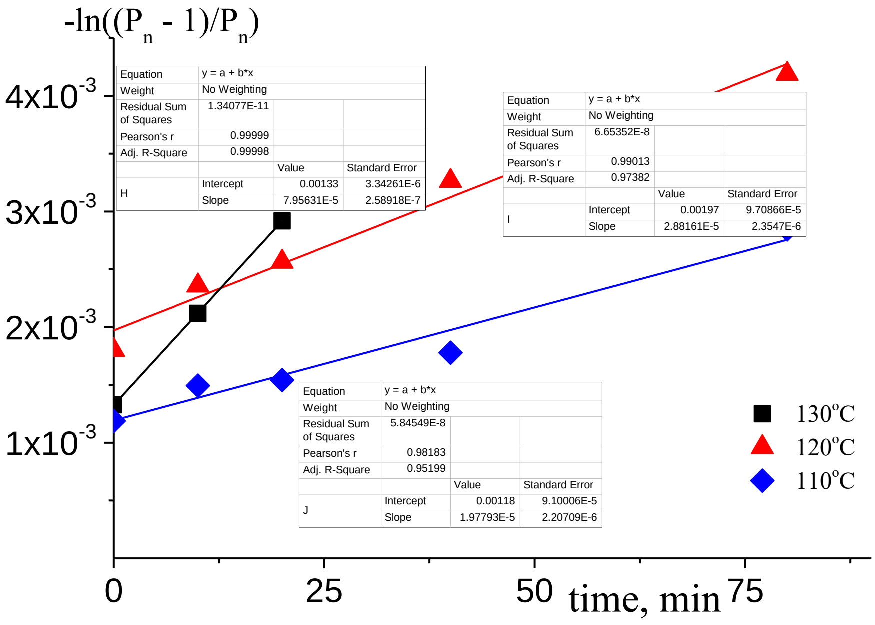


Figure S3. MWDs of initial **PPC** polymerizate (1) and subjected to thermal treatment at (a) 120 and (b) 130°C for 10 (2), 20 (3), 40 (4), and 80 min (5)

Kinetic analysis examines the statistics of bond-breaking processes occurring according to the law of chance. According to [W. Kuhn, https://doi.org/10.1002/cber.19300630631], a long polymer chain with a number of bonds much greater than 1 is considered, in which all bonds of the main chain can be broken randomly, with equal probability.

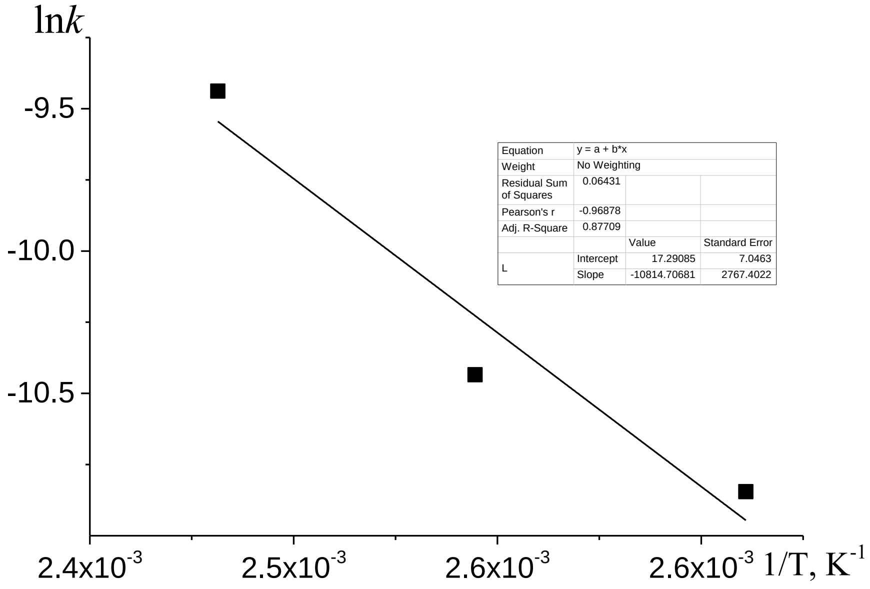


Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1.34077E-11		
Pearson's r	0.99999		
Adj. R-Square	0.99998		
		Value	Standard Error
H	Intercept	0.00133	3.34261E-6
	Slope	7.95631E-5	2.58918E-7

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	6.65352E-8		
Pearson's r	0.99013		
Adj. R-Square	0.97382		
		Value	Standard Error
I	Intercept	0.00197	9.70866E-5
	Slope	2.88161E-5	2.3547E-6

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	5.84549E-8		
Pearson's r	0.98183		
Adj. R-Square	0.95199		
		Value	Standard Error
J	Intercept	0.00118	9.10006E-5
	Slope	1.97793E-5	2.20709E-6

Figure S4. The dependence of P_n of polycarbonate on time during its degradation in the coordinates of Eq. (1) at different temperatures (indicated on the Figure).



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.06431		
Pearson's r	-0.96878		
Adj. R-Square	0.87709		
		Value	Standard Error
L	Intercept	17.29085	7.0463
	Slope	-10814.70681	2767.4022

Figure S5. Semi-logarithmic plot of the degradation rate constant *k* on the reverse temperature.

Degradation in the presence of salen complexes Co(II) and Co(III)

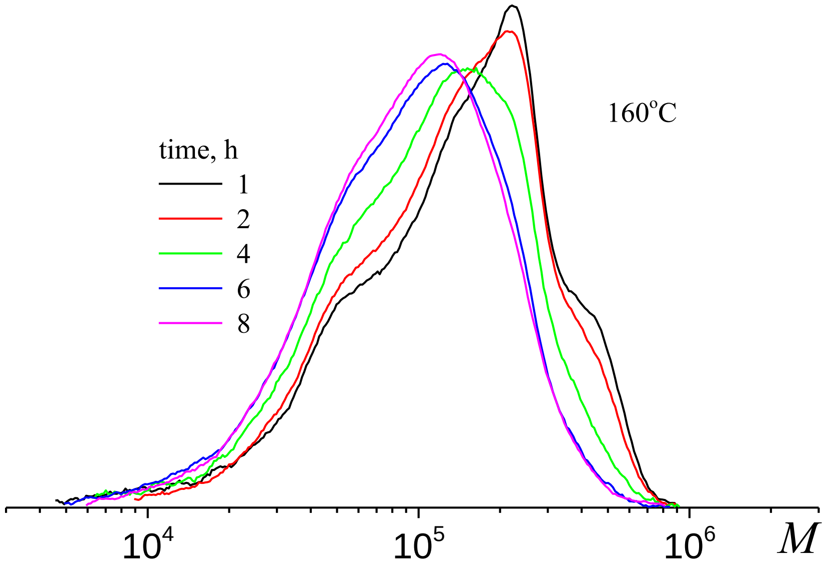


Figure S6. MWD transformation of PPC subjected to thermal treatment in the absence of air at 160 °C.

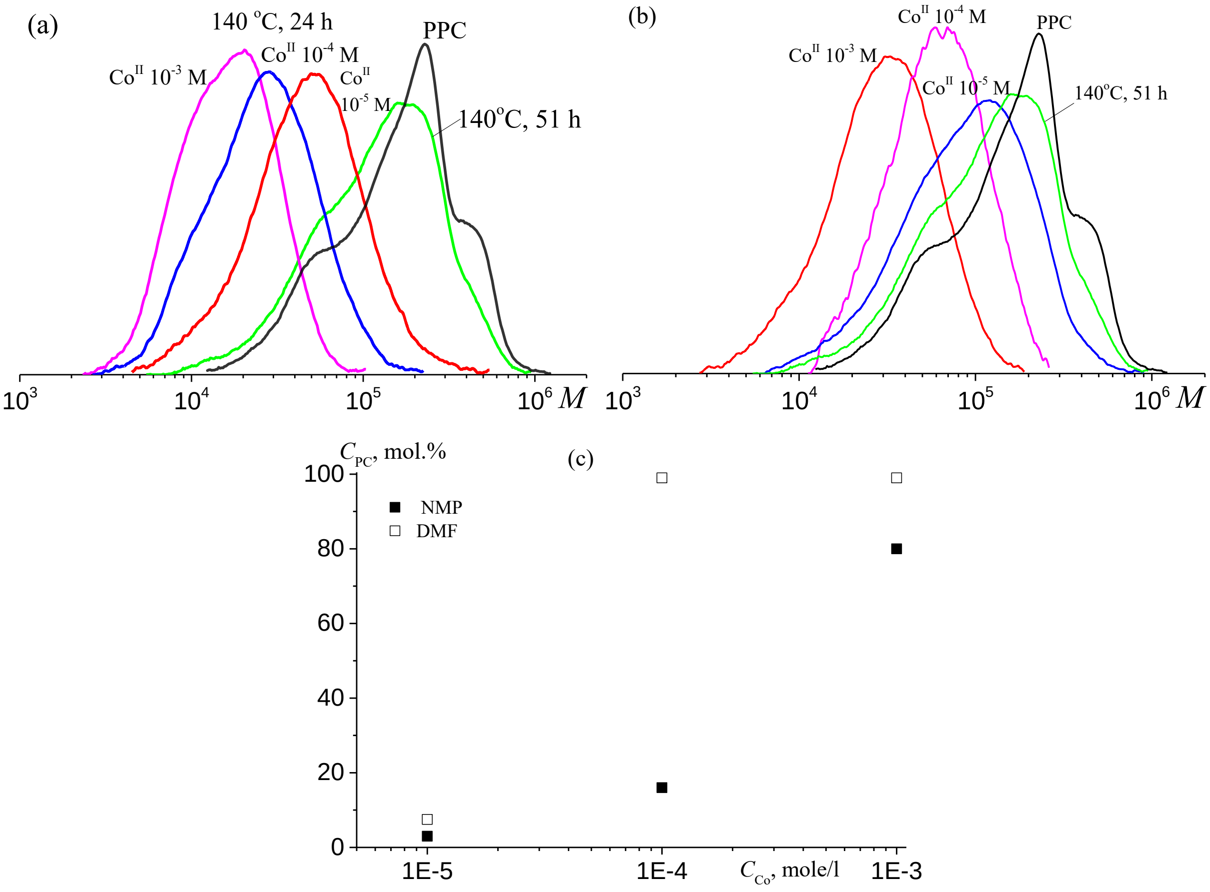


Figure S7. MWD transformation of **PPC** solution subjected to thermal treatment in the absence of air at 140 °C in the presence of salen complex Co^{II} in NMP (a) and DMF (b); dependence of PC released on time during PPC degradation at 140 °C in the presence of various concentrations of salen complex Co^{II} in NMP and DMF.

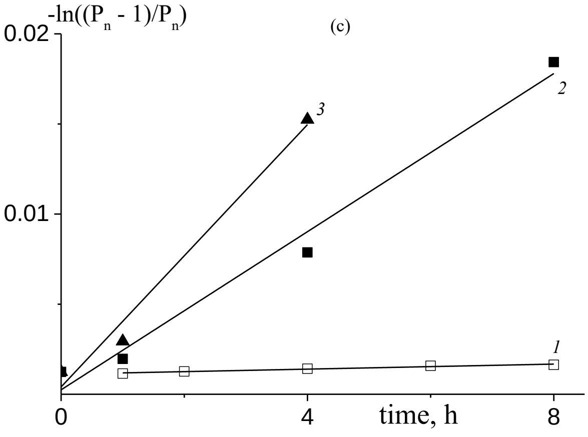
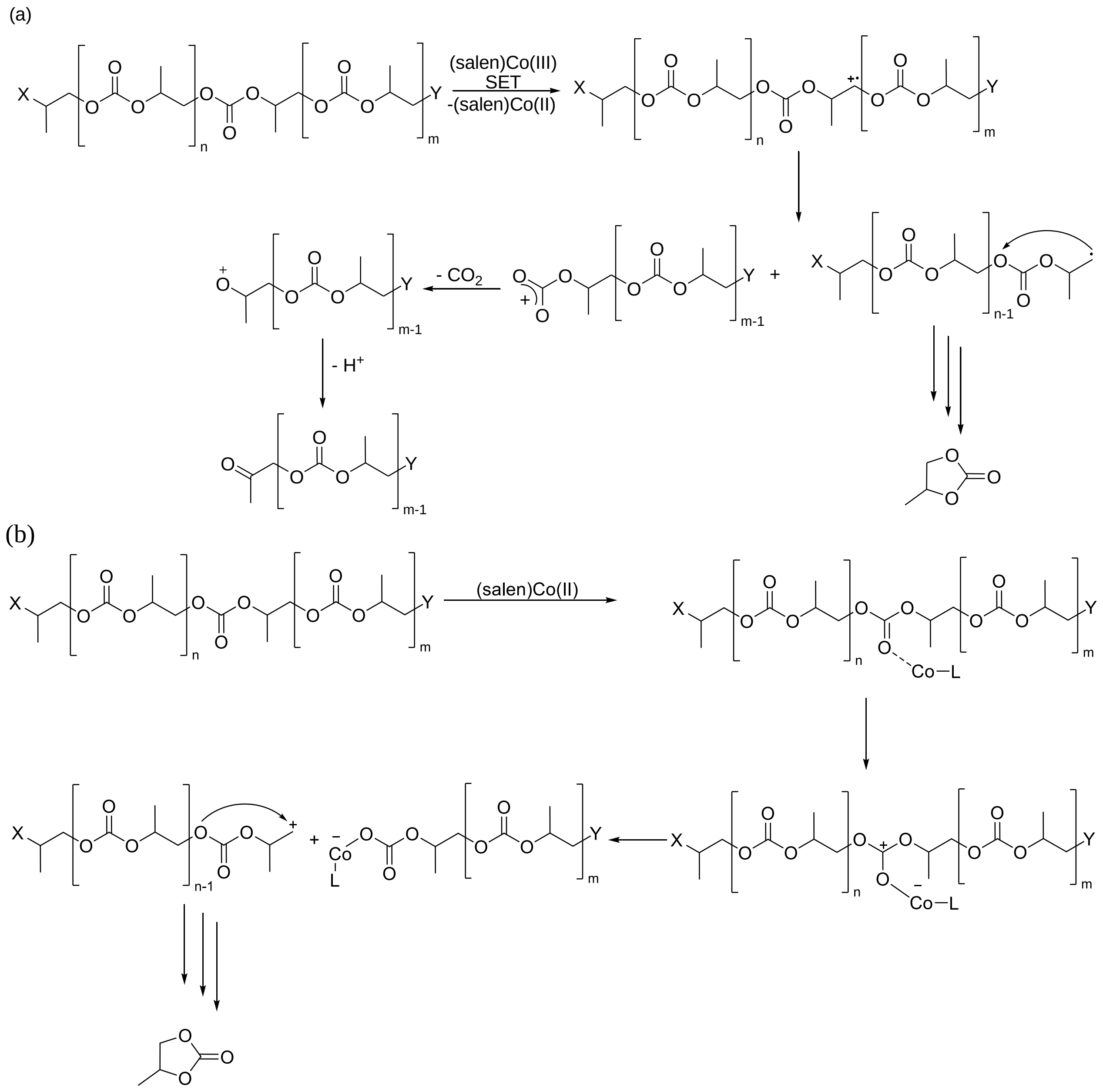
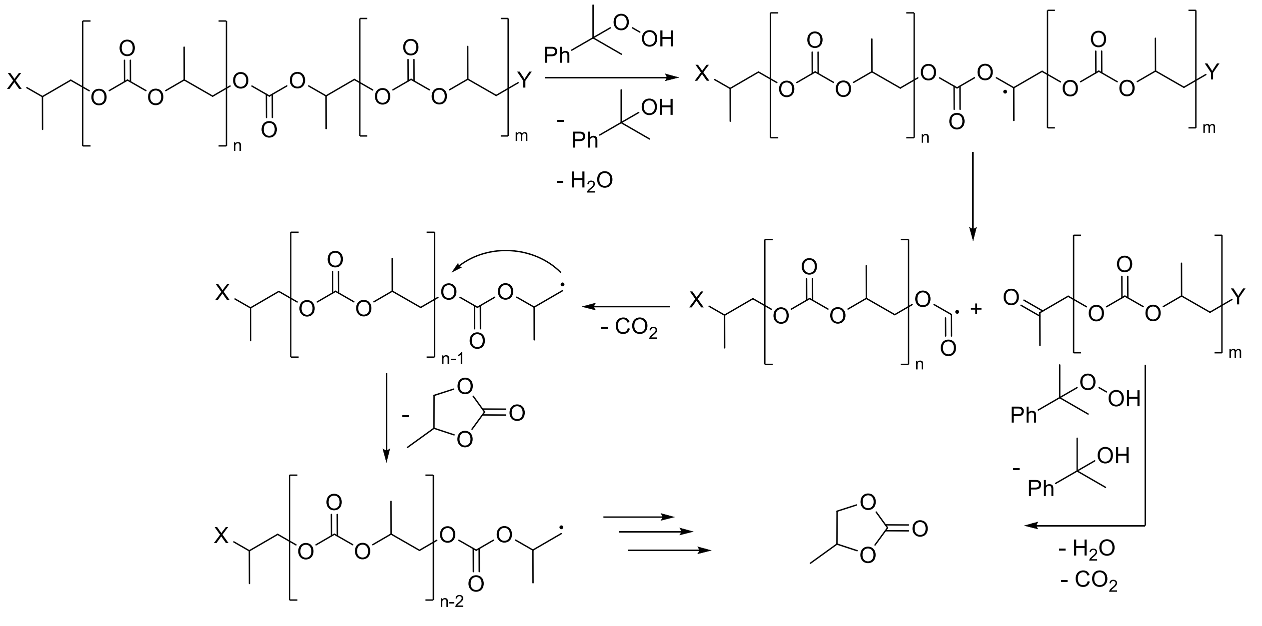


Figure S8. Time-dependence of –ln((P$_n$–1)/P$_n$) (c) for **PPC** subjected to thermal treatment at 160 °C in the absence (1) and in the presence of salen complexes of Co^{II} (2) and Co^{III} (3); medium: in bulk (1), in NMP solution (2, 3).

Proposed mechanisms for the PPC degradation



Scheme S1 Proposed mechanisms for **PPC** destruction under the action of salen complexes of Co^{III} (a) and Co^{II} (b).



Scheme S2 Proposed mechanisms for **PPC** degradation under the action of cumyl hydroperoxide.