Supporting Information for

In-situ Formation of Benzoxazines in Polyoxymethylene: A Simple Approach for Retarding Formaldehyde Generation and Tuning Mechanical Properties under Semi-interpenetrating Network

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Table S1 Conditions to prepare in-situ reactive blend of BA-a in POM together with weight loss, char yield and utilized formaldehyde

Sample	Bisphenol-A (mol)[a]	Aniline (mol)[a]	Weight loss of TGA at 450 °C-600 °C (wt%)	BA-a (mol)[b]	Char yield at 600 °C (wt%)	Poly(BA-a) (mol)[b]	Utilized HCHO (mol)
POM-BA01a02	0.023 (5.25 g)	0.046 (4.28 g)	5	0.008	6	0.008	0.064
POM-BA02a04	0.046 (10.50 g)	0.092 (8.56 g)	8	0.012	10	0.013	0.10
POM-BA03a06	0.069 (15.75 g)	0.138 (12.85 g)	10	0.015	13	0.017	0.13
POM-BA05a10	0.11 (26.25 g)	0.22 (20.48 g)	12	0.018	15	0.020	0.15
POM-BA07a14	0.16 (36.52 g)	0.32 (29.80 g)	15	0.023	18	0.024	0.19
POM-BA10a20	0.23 (52.50 g)	0.46 (42.83 g)	17	0.025	18	0.024	0.20
POM-F04BA01a02 +0.028 mol of CH_2O	0.023 (5.25 g)	0.046 (4.28 g)	3	0.005	6.8	0.002	0.028

[a] Based on mixing with POM (70 g, 2.33 mol of formaldehyde), which generated formaldehyde 1 wt% (0.0233 mol) under 200 °C for 2 h by TGA.

[b] M_w of BA-a: 462.38 $g.mol^{-1}$ and M_w of pol(BA-a) repeating unit: 522.72 $g.mol^{-1}$

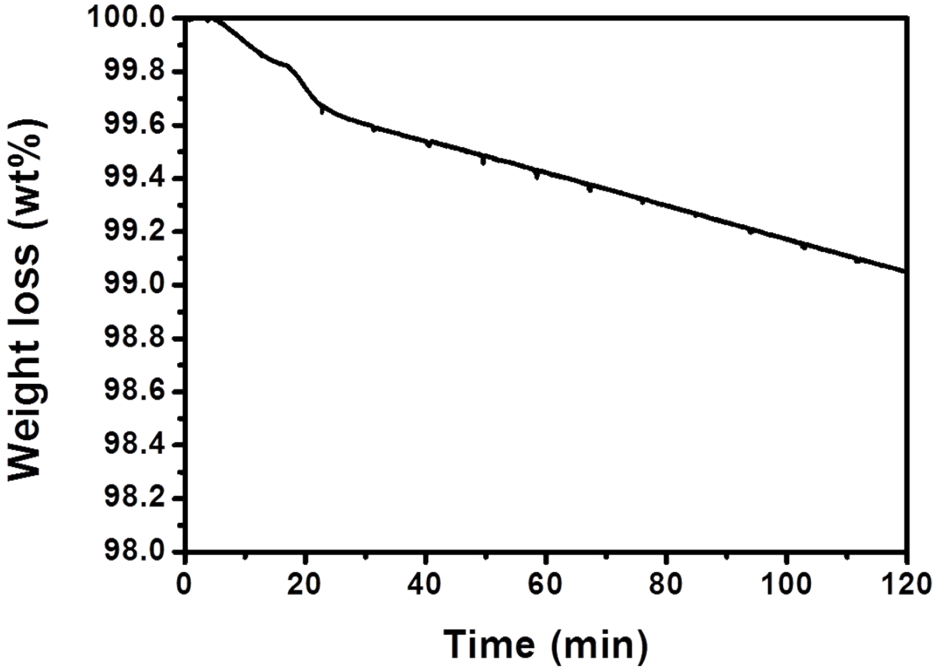

Fig. S1 TGA thermogram of pristine POM in isothermal process at 200 °C.

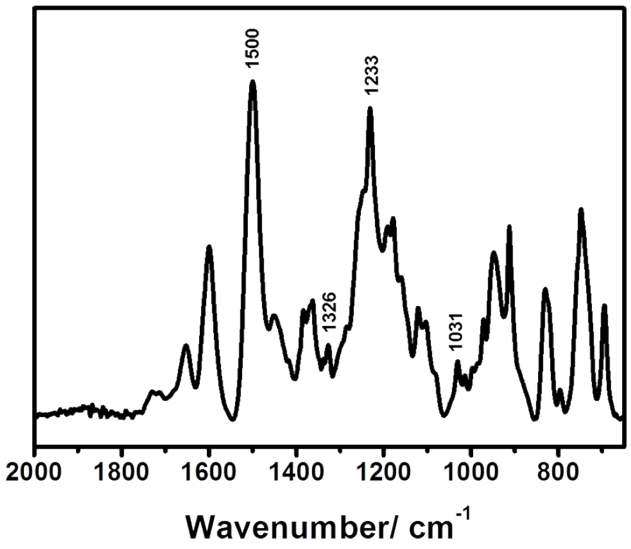

Fig. S2 FTIR spectrum of the precipitates obtained from POM-BA01a02.

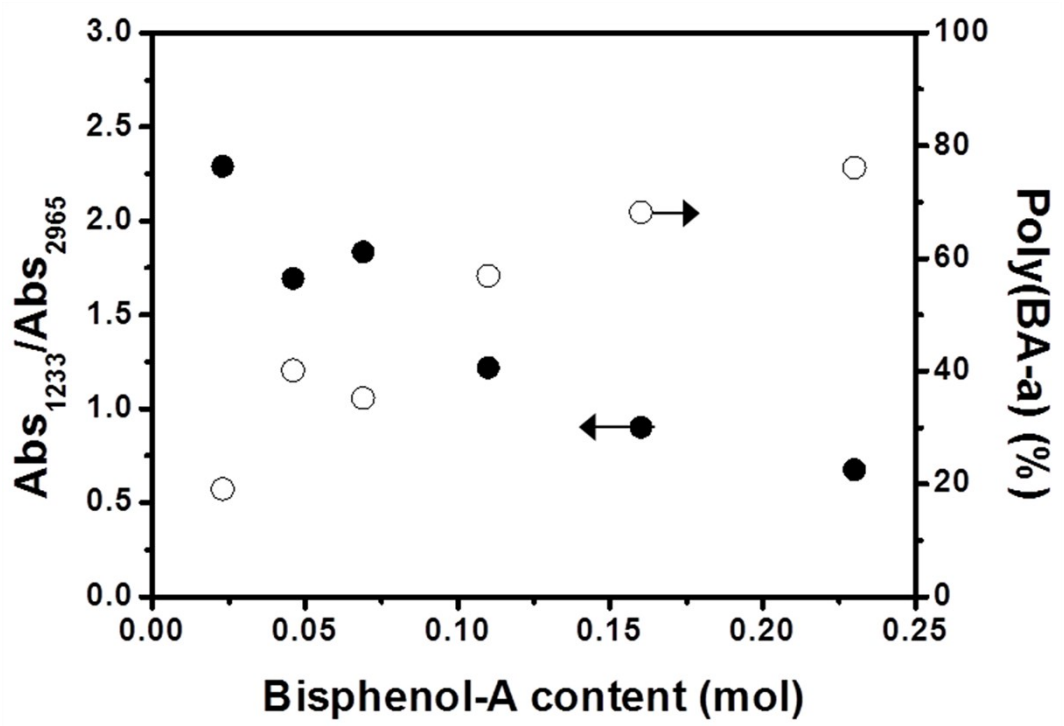

Fig. S3 Integration ratio of C-O-C (1233 cm^{-1}) over those of the CH stretching (2965 cm^{-1}) (●) and poly (BA-a) content (○) as a function of bisphenol-A content.

Table S2 Formaldehyde emission amount (FEA)

Sample	FEA (ppm)
POM	105.3
Direct mixing	
POM (0.33 mol) +Bisphenol-A (0.0033 mol) + aniline (0.0066 mol)	55.3
POM (0.33 mol) +Bisphenol-A (0.0067 mol) + aniline (0.0134 mol)	33.8
POM (0.33 mol) +Bisphenol-A (0.01 mol) + aniline (0.02 mol)	21
POM (0.33 mol) +Bisphenol-A (0.017 mol) + aniline (0.033 mol)	N/A
POM (0.33 mol) +Bisphenol-A (0.023 mol) + aniline (0.046 mol)	N/A
POM (0.33 mol) +Bisphenol-A (0.033 mol) + aniline (0.066 mol)	N/A
Thermally treaded POM	815.13
POM-BA01a02	N/A
POM-BA02a04	N/A
POM-BA03a06	N/A
POM-BA05a10	N/A
POM-BA07a14	N/A
POM-BA10a20	N/A

Mixing in test tube: POM was mixed with bisphenol-A and aniline in the test tube and allowed melting at 200 °C for 2 h. The FEA was collected accordingly.

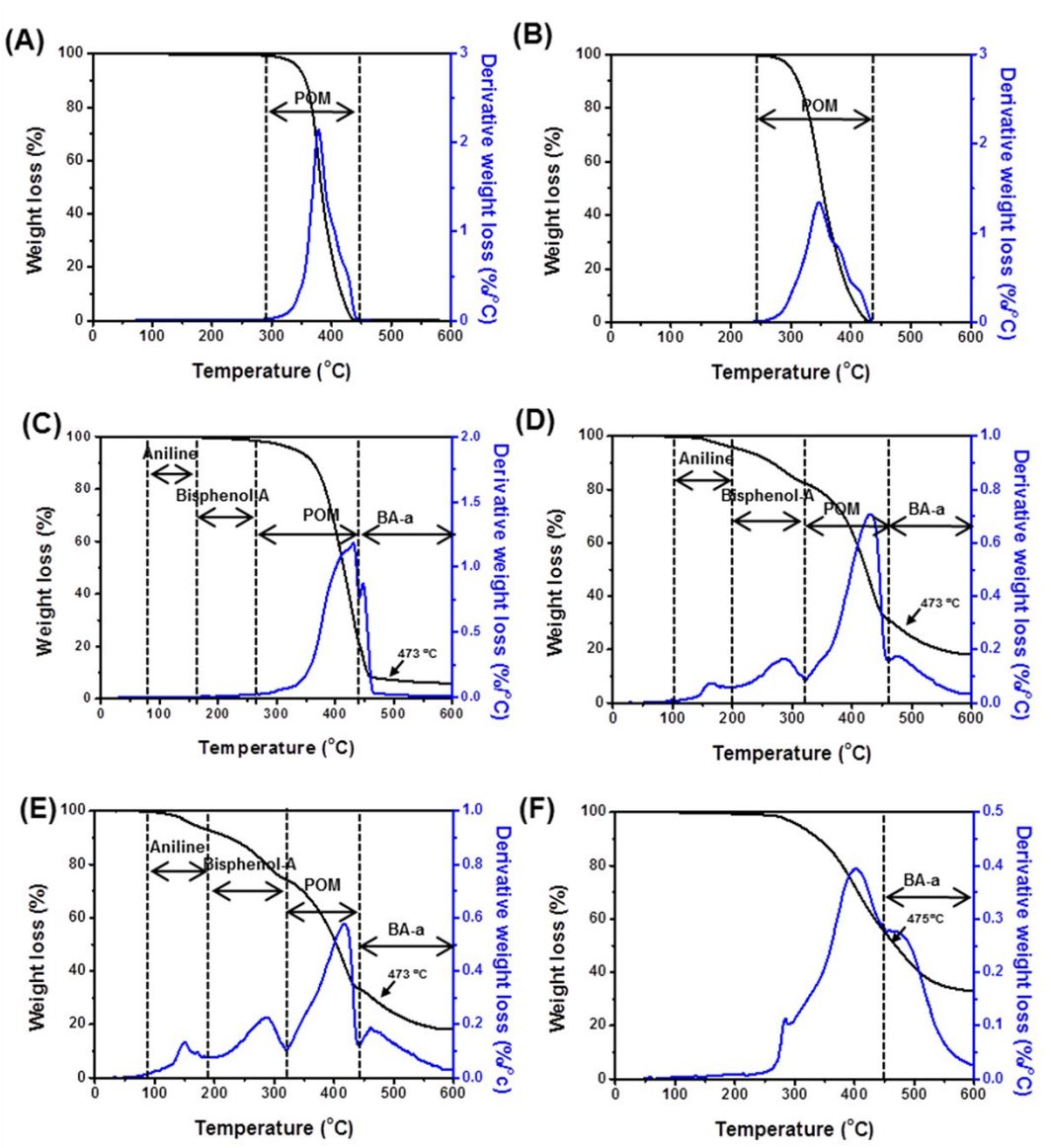

Fig. S4 TGA thermograms of (A) pristine POM, (B) thermally treaded POM, (C) POM-BA01a02, (D) POM-BA07a14, (E) POM-BA10a20 and (F) Poly(BA-a).

Table S3 Weight-averaged molecular weight (M_w), number-averaged molecular weight (M_n) and polydispersity index (PDI) of poly(BA-a) extracted by $CHCl_3$ from POM-BA-a blends.

Sample	M_w[a]	M_n[a]	PDI[a]
POM-BA01a02	1264	909	1.4
POM-BA02a04	1482	934	1.6
POM-BA03a06	1644	937	1.7
POM-BA05a10	1845	922	2.0
POM-BA07a14	3153	1015	3.1
POM-BA10a20	4616	1195	3.8

[a] Weight-averaged molecular weight (M_w), number-averaged molecular weight (M_n), and polydispersity index (PDI)determined by SEC calibrated with polystyrene standard corrected by multiplying with 0.58

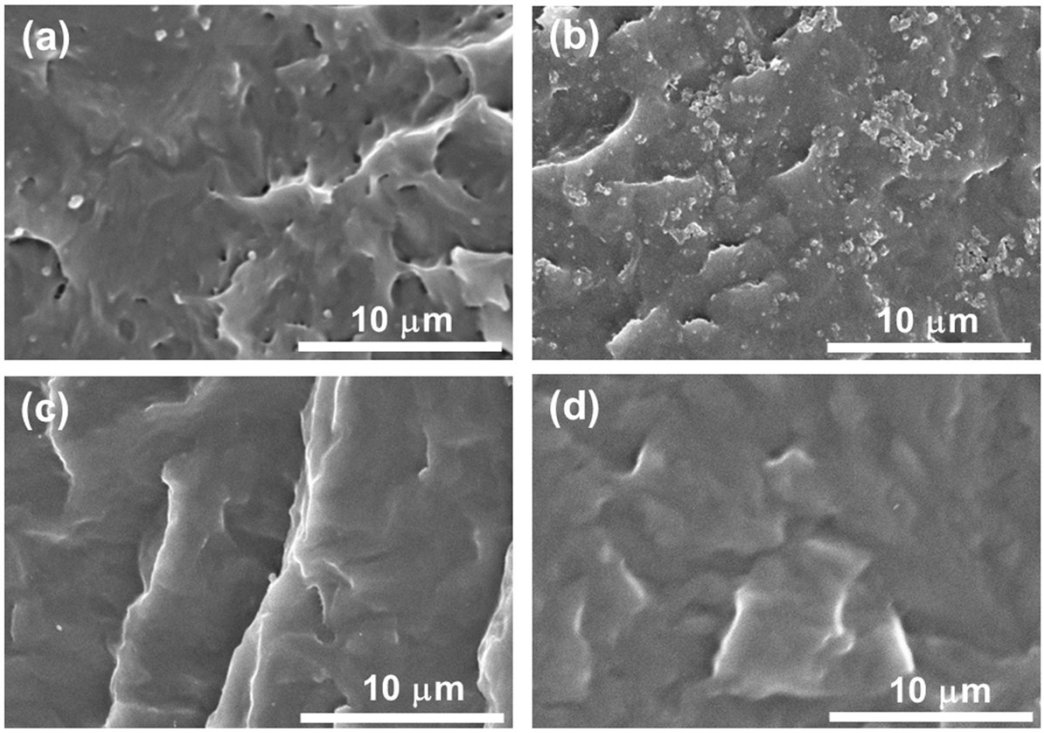

Fig. S5 SEM micrographs of (a) pristine POM, (b) POM-BA03a06, (c) POM-BA07a14 and (d) POM-BA10a20.

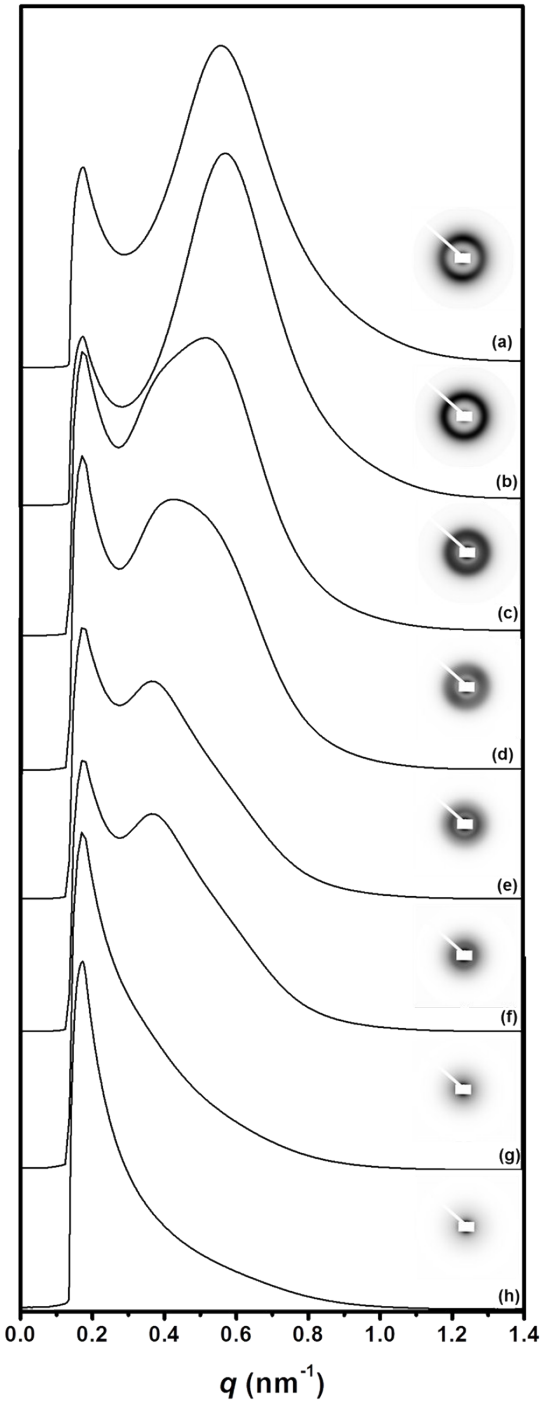

Fig. S6 Circular average SAXS profiles and 2D-SAXS patterns of (a) pristine POM, (b) thermally treated POM, (c) POM-BA01a02, (d) POM-BA02a04, (e) POM-BA03a06, (f) POM-BA05a10, (g) POM-BA07a14 and (h) POM-BA10a20.