



- 1 Supplementary information
- 2 Synthesis of Phosphazene-Containing, Bisphenol A-
- 3 Based Benzoxazines and Properties of Corresponding
- 4 Polybenzoxazines

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Figure S1. ³¹P NMR spectrum of phosphazene-containing benzoxazines at HCP:bisphenol A ratio of
 1:24 (spectra at ratios of 1:12, 1:16, 1:24 are identical).



Figure S2. ¹H NMR spectrum of the phosphazene-containing benzoxazine obtained at a ratio of HCF:
bisphenol A = 1:24.



Figure S3. ¹H NMR spectrum of the phosphazene-containing benzoxazine obtained at a ratio of HCF:
 bisphenol A = 1:16.



Figure S4. ¹H NMR spectrum of the phosphazene-containing benzoxazine obtained at a ratio of HCF: bisphenol A = 1:12.



Figure S5. ESI ⁺ mass spectra of phosphazene-containing benzoxazine. Retention time: A - 13.7 min, B - 15.1 min, C - 16.4 min, D - 17.8 min.

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Figure S6. TGA curves of BA-a and phosphazene-containing benzoxazines based polymers obtained
 in air (a) and in argon (b).

26 TGA description

27 Based on the TGA data (Table 6, the paper) obtained in the air atmosphere (Figure S6a), it can 28 be concluded that the phosphazene component has a small positive effect both on the initial 29 destruction temperatures and on the coke residue. The temperatures of 5% weight loss, compared to 30 BA-a monomer, are 11.5, 19.2 and 17.5 °C higher for samples BP-1, BP-2 and BP-3, respectively. The 31 temperatures of the 10% mass loss, with an increase in the content of the phosphazene fraction, 32 practically do not differ and increased only by 12.2-15.5 °C. However, with an increase in the content 33 of the phosphazene component in the compositions, the nature of the curves slightly differs from the 34 BA-a monomer (Figure 6, Supplementary Information). On the TGA curves there are several 35 characteristic temperature ranges, corresponding, in our opinion:

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1) 310-380 °C corresponds to the destruction of methyl groups in bisphenol A;

2) 350-500 °C presumably corresponds to the destruction of both methylene bridges, methyl
 groups in bisphenol A and, probably, benzene rings of aniline. For BA-a, the temperature of the
 beginning of the transition to the second stage of destruction is 362 °C, and for samples BP-1, BP-2,

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and BP-3 - 395, 372, and 376 °C, respectively. The introduction of phosphazene cycles contributes to
an increase in the temperature of intense destruction, however, the magnitude of this effect varies
nonlinearly with an increase in the content of the phosphazene fraction. This can be explained by the
presence in phosphazene of a different number of cyclolinear oligomers, which negatively affect the
rate of destruction. The highest temperature of intense destruction is characteristic of BP-1.

45 3) 550-600 $^{\circ}$ C – intense oxidation. For BA-a monomer, the transition to intense oxidation occurs

at 558 °C, and for BP-1 samples; BP-2 and BP-3 - 567; 573 and 583 °C, respectively. At this stage, the
most noticeable positive effect of phosphazene, which inhibits the thermal oxidative degradation of

48 the polymer. The most resistant to thermal oxidative degradation were BP-3 and BP-2.

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Table S1. Determining the flammability class of samples according to UL-94 standard.

Sample	Burning duration after the first flame exposure, s	Burning duration after the second flame exposure, s	Drop formation	Flammability class
BA-a	15	3,5	no	V-1
BP-1	11	1	no	V-1
BP-2	3	7	no	V-0
BP-3	7	10	no	V-0

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53 **Figure S7.** ¹H NMR spectrum of the BA-a (region corresponding to aromatic moieties).



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54 Figure S8. ¹H NMR spectrum of the phosphazene-containing benzoxazine obtained at a ratio of HCF:
55 bisphenol A = 1:24 (region corresponding to aromatic moieties).





56 Figure S9. ¹H NMR spectrum of the phosphazene-containing benzoxazine obtained at a ratio of HCF:
57 bisphenol A = 1:16 (region corresponding to aromatic moieties).

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59 Figure S10. ¹H NMR spectrum of the phosphazene-containing benzoxazine obtained at a ratio of HCF:
60 bisphenol A = 1:12 (region corresponding to aromatic moieties).

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