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Functionalized Oligoaryloxycyclotriphosphazenes and Noncombustible Binders Based on Them

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Abstract—Carboxyl-containing aryloxycyclotriphosphazene (I) has been used for curing the ED-20 epoxy resin or a phosphazene-containing epoxy oligomer. In the case of ED-20, curing occurs in the range of 125–220°C and is accompanied by an exothermic effect that increases from 26 to 50 J/g with an increase in the amount of aryloxycyclotriphosphazene (I) from 25 to 50%. The curing of the phosphazene-containing epoxy oligomer occurs in the temperature range of 140–240°C and is accompanied by an endothermic effect ($-\Delta H = 6.5$–6.8 J/g). Cured compositions based on ED-20 + I are self-extinguishing (flammability class V-1 according to UL-94), and phosphazene-containing epoxy oligomer + I compositions are noncombustible (class V-0 according to UL-94) regardless of the ratio of the initial components.

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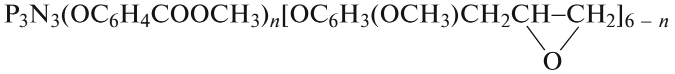
In recent years, efficient methods have been developed for the synthesis of phosphazene-containing epoxy oligomers (PEOs), which are of interest for the fabrication and modification of polymer composite materials [1–5]. Functionalized aryloxycyclotriphosphazenes with carboxyl [6, 7] or epoxy groups [8–10] are particularly promising for these purposes.

In [11] we described the synthesis of mixed aryloxycyclotriphosphazenes containing carboxyl or epoxy groups in aromatic radicals bound to phosphorus atoms:

I – $P_3N_3(OC_6H_4COOH)_n[OC_6H_3(OCH_3)CH_2CH{=}CH_2]_{6-n}$

II –

$$P_3N_3(OC_6H_4COOCH_3)_n[OC_6H_3(OCH_3)CH_2\underbrace{CH{-}CH_2}_{O}]_{6-n}$$

In this paper, we present data on the use of oligomer I for curing organic epoxides, PEO, and oligomer II. In the last two cases, the phosphorus content in the reactant mixture and in the resulting composite is 7–8%, which should ensure the incombustibility of the latter.

EXPERIMENTAL

An epoxy resin of the brand ED-20 manufactured by the Sverdlov plant (Russia; GOST 10587-84) was used without further purification; its epoxy value is 19–21.

Tris(4-carboxyphenoxy)tris(4-allyl-2-methoxyphenoxy)cyclotriphosphazene (I) was obtained according to the procedure described in [11]. The product was a brown viscous liquid containing compounds I with n = 3 (24%) and 2 (76%) according to laser mass spectrometry data. ^{31}P NMR spectrum: $\delta_p = 9.8$ ppm.

Tris(4-carbonylmethoxyphenoxy)$_n$tris(4-epoxy-2-methoxyphenoxy)$_{6-n}$cyclotriphosphazene (II) was also synthesized as described in [11]. According to laser mass spectrometry data, the product contains compounds with n = 3 (38%) and 2 (48%). ^{31}P NMR spectrum: $\delta_p = 9.8$ ppm; the epoxy value is 11–13%.

Mixtures were prepared by mixing the initial components at 25–30°C for 4 h using an overhead stirrer to uniformly distribute the components and degassed in a vacuum for 5 h.

The compositions were cured by heating in air at 200–250°C for 4–10 h. The completeness of curing was estimated from the amount of the gel fraction determined in a Soxhlet apparatus using acetone as the solvent.

Table 1. Main compounds in the products of reactions (1) and (2) according to MALDI-TOF mass spectrometry data

Reactants	*m*/*z*	Compound formula	Relative amount of compound in products, wt %
$P_3N_3(OPar)_6$	1064	$P_3N_3(OPar)_6Na^+$	68
	1080	$P_3N_3(OPar)_6K^+$	20
	1090	$P_3N_3(OPar)_6Na^+Na^+$	12
$P_3N_3(OPar)_6$ + EvgONa (molar ratio 1 : 3.5)	1064	$P_3N_3(OPar)_6Na^+$	28
	1076	$P_3N_3(OPar)_3(OEvg)_3$	36
	1100	$P_3N_3(OPar)_3(OEvg)_3Na^+$	19
	1136	$P_3N_3(OEvg)_6Na^+$	17
$P_3N_3(OEvg)_6$	1113	$P_3N_3(OEvg)_6$	35
	1136	$P_3N_3(OEvg)_6Na^+$	57
	1152	$P_3N_3(OEvg)_6K^+$	8
$P_3N_3(OEvg)_6$ + ParONa (molar ratio 1 : 3.3)	1100	$P_3N_3(OPar)_3(OEvg)_3Na^+$	4
	1113	$P_3N_3(OEvg)_6$	13
	1123	$P_3N_3(OPar)_3(OEvg)_3Na^+Na^+$	3
	1136	$P_3N_3(OEvg)_6Na^+$	69
	1152	$P_3N_3(OEvg)_6K^+$	11

The TGA and DSC curves were recorded on a NETZSCH STA 449 F3 Jupiter + QMS 403 Aeolos Quadro high-temperature simultaneous thermal analyzer at a heating rate of 10 K/min in air using a sample size of 10 mg.

The MALDI-TOF mass spectra were recorded on a Bruker AutoFlex II instrument.

RESULTS AND DISCUSSION

It was previously noted that there was a discrepancy between the product composition and the amount of the reactants in the reaction mixture in the case of synthesis of compounds I and II by successive substitution of the corresponding phenolates for chlorine atoms in hexachlorocyclotriphosphazene [11]. It has been suggested that the aryloxy groups already bound to the phosphorus atoms may be transesterified to the residues of another phenol.

Since such reactions are also possible during curing, their occurrence can change the composition of the initial aryloxycyclotriphosphazenes and the parameters of the resulting composite. In order to confirm this assumption, the following model reactions were carried out:

$$P_3N_3(OC_6H_4COOCH_3)_6 + NaOEvg \rightarrow P_3N_3(OC_6H_4COOCH_3)_{6-x}(OEvg)_x, \quad (1)$$

$$P_3N_3(OEvg)_6 + NaOPar \rightarrow P_3N_3(OEvg)_y(OPar)_{6-y}. \quad (2)$$

Here, Evg and Par are the eugenol and paraben residues, respectively.

A MALDI-TOF analysis of the products of reaction (1) shows (Fig. 1) a significant decrease in the proportion of paraben radicals and an increase in the amount of mixed derivatives (Table 1). It is surprising that up to 17% of the hexaeugenol derivative was found in the product of reaction (1), indicating the complete replacement of the paraben radical by the eugenol one.

The opposite picture is observed in the case of reaction (2). The laser mass spectrum of the product of this reaction (Fig. 2) contains only two peaks of insignificant intensity corresponding to compounds with equal amounts of both phenol residues (three for

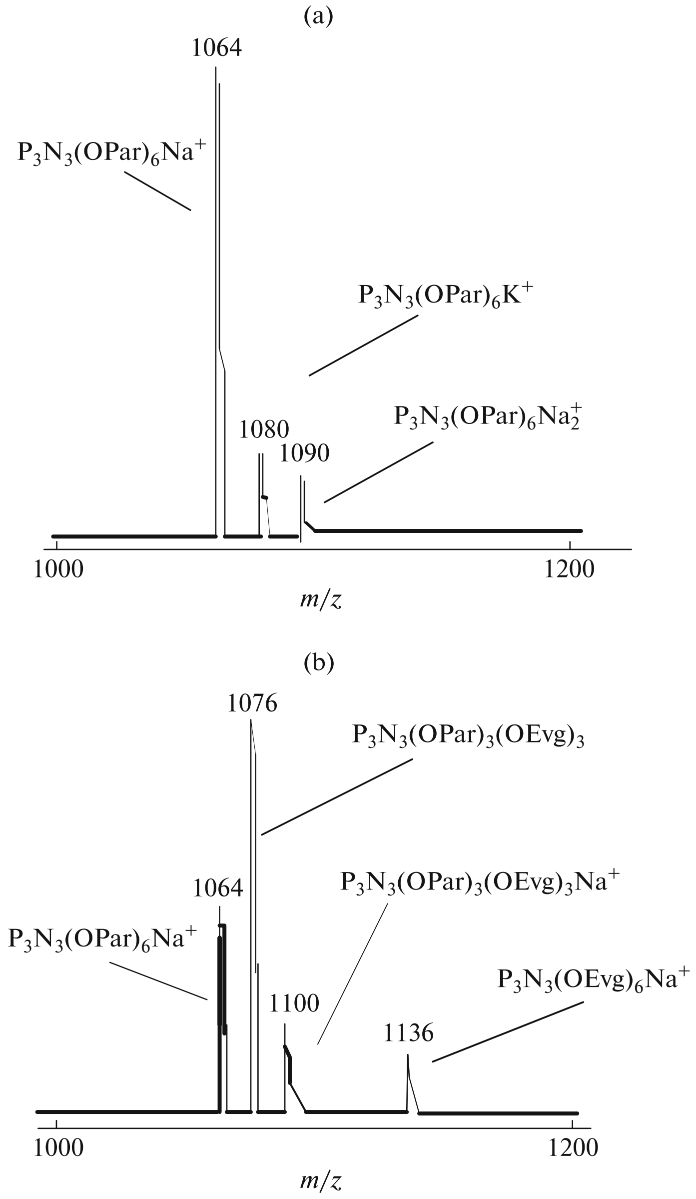


Fig. 1. MALDI-TOF mass spectra of (a) the reactant $P_3N_3(OPar)_6$ and (b) the product of its reaction with eugenol at a molar ratio of 1 : 3.5. Synthesis in a dioxane medium at 102°C for 8 h.

each). The proportion of these compounds does not exceed 7%, and they do not include substances with one or two paraben radicals, which may mean a higher reactivity. This circumstance is indirectly confirmed by a low amount of compounds having a number of various aryloxy radicals close to three in the products of both reactions (Table 1).

The curing of ED-20 + I and II + I compositions with different amounts of the initial components was carried out at 200°C for 4–6 h, i.e. the time required for the quantitative formation of the gel fraction (Fig. 3). Curing in this case occurs due to the interaction of carboxyl groups of oligomer I and epoxy groups of ED-20 resin or oligomer II [12]. The amount of the gel fraction increases faster in the II + I system than in the ED-20 + I mixture. In our opinion, this is due to a stronger intermolecular interaction of phosphazene components of the same nature.

Allyl double bonds in oligomer I do not participate in the curing reaction, but they are subject to oxidation by peracids during the formation of oligomer II. Their content can be easily determined from the laser mass spectra given in [11] or calculated from the epoxy value of oligomer II if necessary.

This fact also confirms the independence of the degree of curing of the II + I system with different

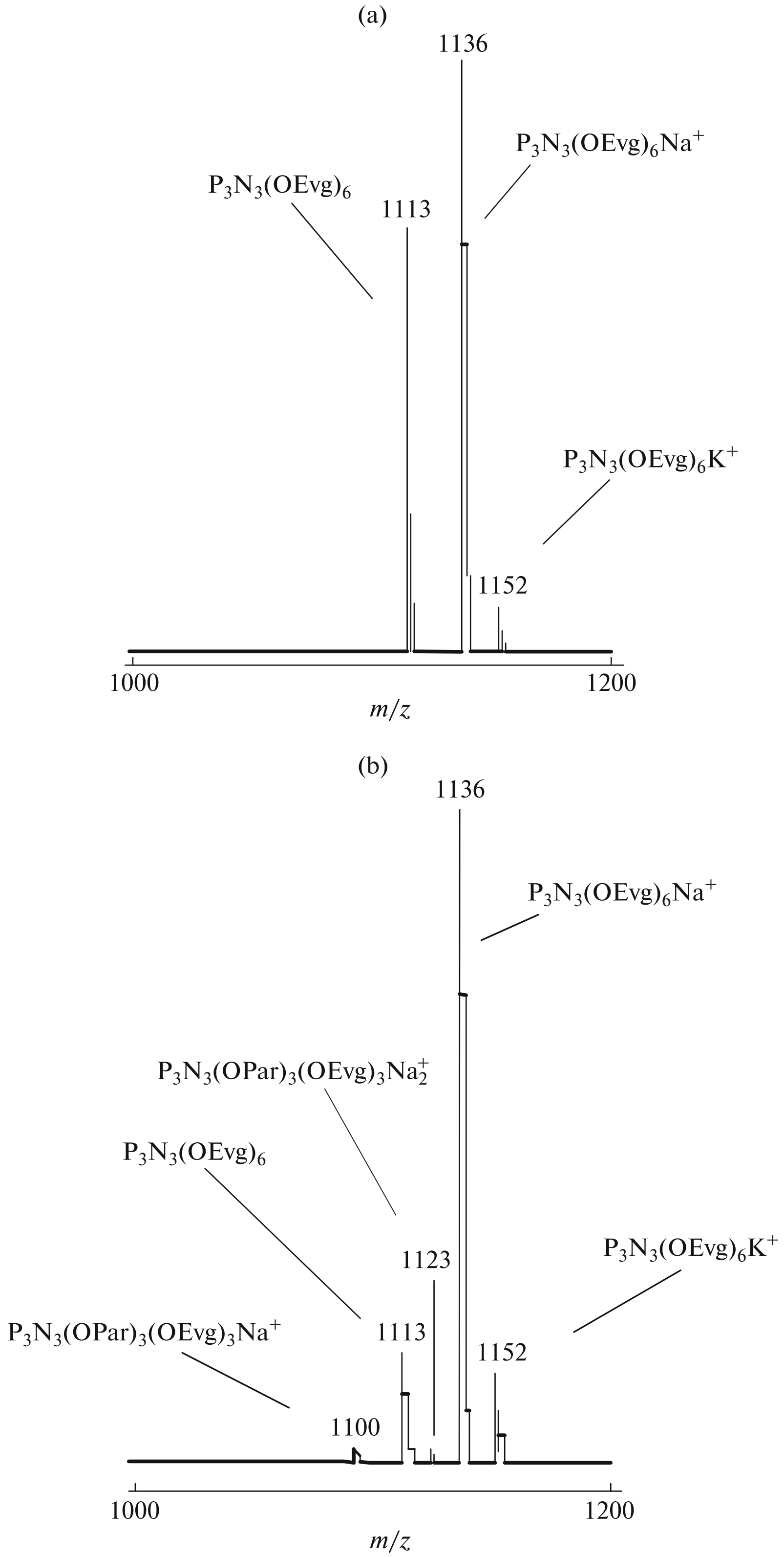


Fig. 2. MALDI-TOF mass spectra of (a) $P_3N_3(OEvg)_6$ and (b) the product of its reaction with the Na derivative of methylparaben at a molar ratio of 1 : 3.3. Synthesis in acetone at 64°C for 8 h.

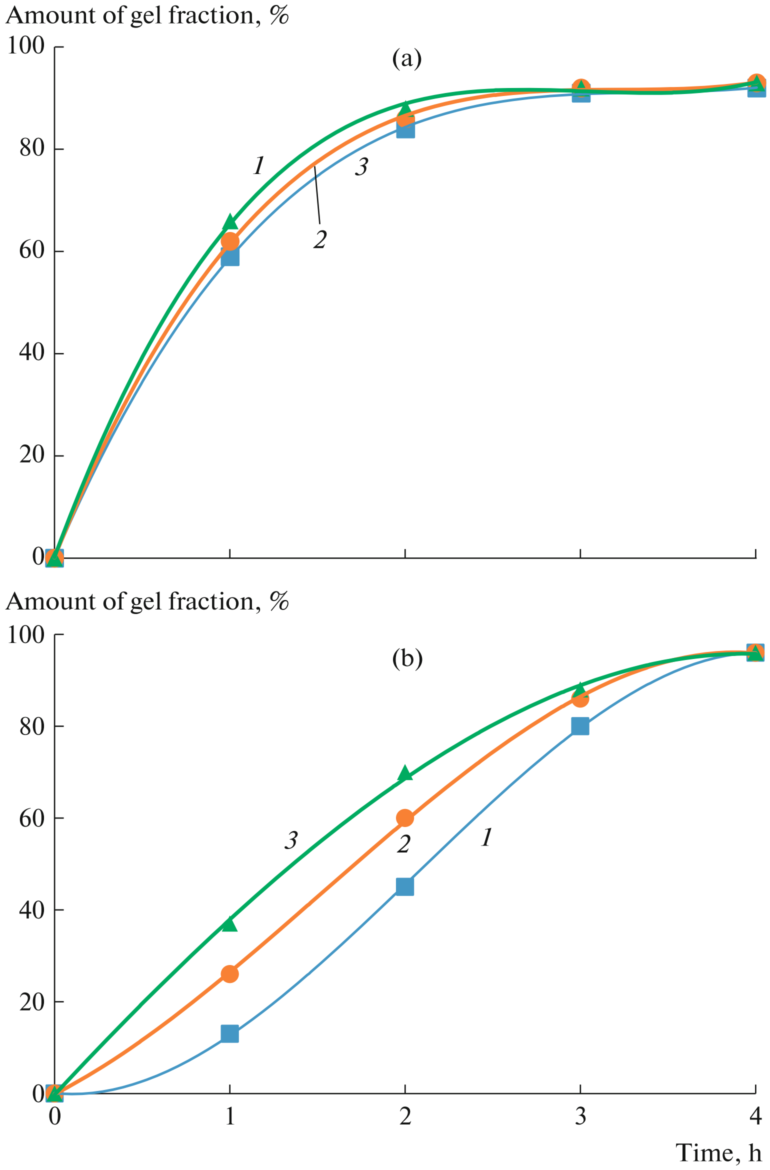


Fig. 3. Change in the amount of the gel fraction during the curing of (a) II + I and (b) ED-20 + I mixtures. Mass fractions of component I in the mixture with epoxides were (a) (*1*) 75, (*2*) 50, or (*3*) 25% and (b) (*1*) 15, (*2*) 20, or (*3*) 35%.

amounts of the components in the initial mixture within the limits of their relative amount of 25–75 wt %.

Curing was also monitored by TGA and DSC; the results are presented in Tables 2 and 3. The curing of the ED-20 + I system is accompanied by exothermic effects with a ΔH value of not more than 50 J/g. According to DSC data, the curing temperature of this system is in the range from 125–140 to 210–220°C.

The weight loss is insignificant in this range, indicating minimal side transformations, in particular, the absence of decarboxylation. In contrast to the ED-20 + I system, a mixture of two phosphazene components (II + I) cures endothermically with thermal effects of $-\Delta H \sim 6$ J/g. The reason for such an unusual behavior is not yet clear and requires a special study.

Cured compositions based on ED-20 + I with the concentration of I more than 30% are self-extinguishing; the II + I compositions with the concentration of carboxyl-containing component I from 30 to 75% are completely noncombustible (flammability class V-0 according to UL-94); i.e., there is self-extinguishing of vertically and horizontally fixed samples after they are removed from the burner flame.

Table 2. Temperature intervals of peaks in the DSC curves for ED-20 + I systems

Amount of component I in mixture, wt %	Temperature, °C			ΔH, J/g
	peak onset	value at maximum	peak end	
15	no peaks			–
20	–	190*	–	–
25	140	190	225	28
30	125	190	220	40
35	125	180	210	52
50	125	180	210	50

* Inflection in the DSC curve.

Table 3. Parameters of TGA and DSC curves for II + I systems

Amount of component I in mixture, wt %	Weight loss, %		Temperature, °C			$-\Delta H$, J/g
	at 200°C	at 250°C	peak onset	value at maximum	peak end	
0*	8	16**	–	–	–	–
25	–	–	–	–	–	6.5
50	6	12	140	150	230	6.7
75	5	10	150	160	245	6.8
100	5	8	–	–	–	–

*Epoxide II.

**Weight loss at 540°C is 71%.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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