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Degradation Heterochain Polymers in the Presence of Phosphorus Stabilizers

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The thermal stability and thermal stabilization of the heterochain polymers were investigated. Analysis of PAI, PSF, PEI degradation and stabilization has allowed an approach to be developed to aid their processing and resolve similar problems with other resins such as polyethersulfone, LCP, etc. Addition of PCA inhibits in heterochain polymers thermal oxidation at high and low temperatures.

Keywords Cyclization; hindered phosphate; liquid-crystal copolyesters; polyesterimides; polyimides; polysulfones; pyromellite imide

Introduction

Analysis of data from the literature and the authors' investigations indicate injection of phosphorus-containing additives (PCA) in polymers as the most perspective way of heat-resistant polymer thermal stabilization [1–20]. Tests of a wide PCA range in different polymer structures (aromatic and fatty-aromatic polyamides and polyimides, polyesterimides, polyamidoimides, polysulfones, liquid-crystal copolyesters, etc.) allowed selection of optimal thermostabilizing additives: aromatic esters and phosphorous and prosphoric esteramides. For pure aromatic polyimides, polyimidophenylquinoxalines and polybenzoxazoles, optimal concentrations are 3 wt.% PCA. At equal heat loads, properties of stabilized samples are 1.5–2.5 times higher compared with non-stabilized polymers. For aliphatic-aromatic polymers (bisphenol A-derived polysulfone and polyesterimide, polyalkane imide, and polyphthalimides), PCA optimal concentrations are two times lower: 0.3–1.0 wt.%. This is caused by lower temperature impacts during processing and operation of materials and articles.

To develop the idea of heat resistant polymer stabilization, one must understand the mechanism of PCA stabilizing action in them. At the same time with stabilization applied in manufacturing of polymers, some studies were performed before on the example of aromatic polyimides. The inhibiting action of PCA on oxidation branch of degradation was detected while the pre-polymer cyclization rate increased in PCA

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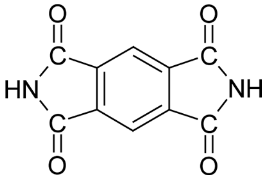
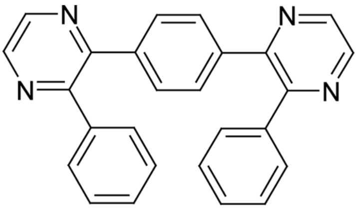
presence. It was also found that crosslinking processes are intensified on the initial stages of thermal oxidation.

Experimental data indicate a complex mechanism of PCA action in heat-resistant polymers, which includes inhibition of radical chain reactions and catalysis of cyclization and crosslinking processes.

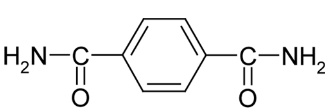
The comparison data on kinetics of inhibited and non-inhibited oxidation of polypyromellitimide, PAI, PPA, PEI, and PSF at high processing temperature and in solid oxidation show general tendencies. In both cases, kinetic curves of oxygen absorption and main oxidation products release (carbon oxides) may be conditionally divided into two stages: the initial stage obeying kinetic order one and have the constant rate. Inhibition of thermal oxidation is observed at the first stage of heat-resistant polymer degradation. For example, rate constants of oxygen absorption by PI equal $7.5 \times 10^{-7} - 1.6 \times 10^{-5}$ and $1.9 \times 10^{-6} - 7.4 \times 10^{-8}\,s^{-1}$ for non-stabilized and stabilized PI, respectively. Gas products release demonstrates similar relations. A decrease of thermal oxidation solid product (pyromellite imide, PDI) yield was also observed – by 2.5 times for PI and 5 times for PAI:



Injection of PCA to polyphenylquinoxalines significantly decreases the yield of analogous (in relation to the polymer structure) product, which is N-phenylpyrazine:



Correspondingly, in PPA [20] the yield of therephtalic amide is almost eliminated (during the studied time period up to 5.000 h).



The amounts of PDI and analogous products (relative to polymer structures) [3,19] indicate the conversion degree in oxidation transformations. The absence of these compounds in degradation products after reaction without oxygen testifies about exclusively thermal oxidation origin of their formation. Therefore, stabilization of heat-resistant polymers (HRP) displays clear antioxidant type, i.e., an additive is able of interacting with radicals and other labile products of HRP thermal oxidation.

High-temperature activity of PCA in radical reactions is additionally confirmed by stabilizing effect of anilide phenyl phosphate (APP) on PE degradation at 300°C. Application of such a model system to this particular case is desirable, because the radical-chain type of PE thermal oxidation at 200–250°C is well-known. It is also forecasted well for higher temperatures and, therefore, at some chain branching degree is forecasted well for carbonyl structures.

A significant contribution of the branching degree to polymer properties, including thermal stability, was shown by Korshak [21]. Non-cyclic units represent the main element of branching [3,22]. The PCA effect on the cycle formation process was assessed using gas-chromatographic analysis of water release from polyamidoacid films – PI and PEI pre-polymers. Intensive water release was observed at initial cyclization stages at 150–200°C. Total water amount released from stabilized and non-stabilized PI and PEI at 250–300°C are nearly the same, i.e., in both cases, cyclization degrees are close. The PCA effectiveness for polyphenylquinoxaline – the polymer, in which cyclization proceeds easily, without any additional heat treatment – indicates that cyclization process acceleration in heat-resistant polymers (PI, for example) may not explain the protective action of PCA.

Another possible stabilization mechanism – the formation of more stable network polymer structure in the presence of PCA with hindered oxygen access – was checked using the spin probe technique [23]. The probe (nitroxyl radical) diffusion into PI matrix was traced by changes in ESR spectra from classical triplet of freely isotropic-rotating, stable nitroxyl radical to a triplet degenerate by boundary components, typical of a probe rotating in a viscous medium. The spectrum (Fig. 1) is of superposition type and indicates the presence of slow (main) and fast

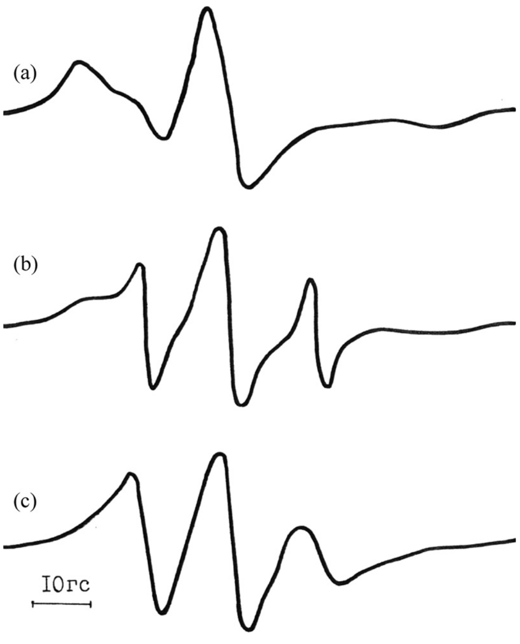


Figure 1. ESR spectra of spin probe in PI film without additives (a, c) and added by APP (b); a, b – prior to thermal aging; c – after thermal aging at 300°C during 500 h in air.

probe motion zones in the polymeric matrix. Relaxation times for non-stabilized and stabilized PI films were determined from graphic charts [41] as follows: $\tau_1 = 2 \times 10^{-8}$, $\tau_2(\sim 5\%) = 10^{-9}$ s and $\tau_1 = (2+5) \times 10^{-8}$, $\tau_2(\sim 10 + 15\%) = 10^{-10}$ s, respectively. These values indicate a definite plasticizing effect of the additive on PI film properties. After thermal aging of films at 300°C during 500 h, τ_1 does not increase. Vice versa, for non-stabilized sample it decreases to 10^{-9} s, whereas for stabilized sample it remained practically unchanged. Apparently, the decrease of τ_1 in non-stabilized film is associated with probe fixing on structure defects (various microcracks), but not with molecular mobility increase.

Degraded non-stabilized PI possesses self paramagnetic properties (a singlet with $\Delta H \approx 10E$), which superimposes on the central component of ESR spectrum of the probe. This contribution is negligible for stabilized sample. The behavior of paramagnetic probe definitely reflects molecular mobility of the solid. Moreover, rotational and translational diffusion of the probe correlates with the behavior of other "small" molecules (oxygen, for example) in the solid matrix. As observed in the experiment, additional crosslinking does not cause a noticeable change in molecular mobility of the polymer and hindrance of O_2 diffusion inside the sample.

The effective method for increasing thermal oxidation stability of polymers is the control of the physical structure [23]. The additive effect on the physical structure of PI film was studied with the help of X-ray structural analysis. The film possesses mesomorphous regularity, of which the presence of an intrachain order in the absence of interchain packing regulation is typical. As shown on the diffraction patterns, such structure manifests itself by a single narrow peak of the intrachain order (5–6 deg.) and wide amorphous halo (Fig. 2). Diffraction patterns show high intrachain orderliness of the stabilized sample. This difference is preserved still after 1,000 h of aging at 300°C at total reduction of the intrachain order. Similar situation is observed on diffraction patterns for liquid-crystal polymers (Fig. 3), stabilized by cyclic phosphites derived from pentaerythtitol Irgafos 126 (Ciba). However, stabilization may just partly be associated with the intrachain order increased in the presence of PCA. PCA are also effective in amorphous polymers, such as PSF and PPQ [3].

As shown by the experiment, crosslinking proceeding during aging of PI films, both stabilized and non-stabilized, does not cause any significant change in molecular mobility of the polymer and hindrance of oxygen diffusion deep in the sample. Crosslinking intensification by PCA injection is disproved by the data on PAI and PPA melt viscosities which decrease in the presence of PCA.

The studies performed with industrial and model PAI, PPA, PEI, and PSF samples, aimed at determination of PCA action as deactivators of admixtures in heat-resistant polymers yielded positive results.

PSF high-temperature oxidation is slowed down by low PCA additions. Although organic phosphites, especially HP, are of the highest efficiency and their stabilizing action is spread upon the whole complex of degradation manifestations, other PCA classes, even red phosphorus, are positively active, mostly stabilizing color.

Analysis of the literature data [24–36] concerning phosphite activity at low-temperature oxidation (initiated self-induced oxidation of hydrocarbons and polyolefins) and behavior of polymers with phosphorus-containing additives at pyrolysis in the sub-flame zone indicates possible mechanisms of phosphorus

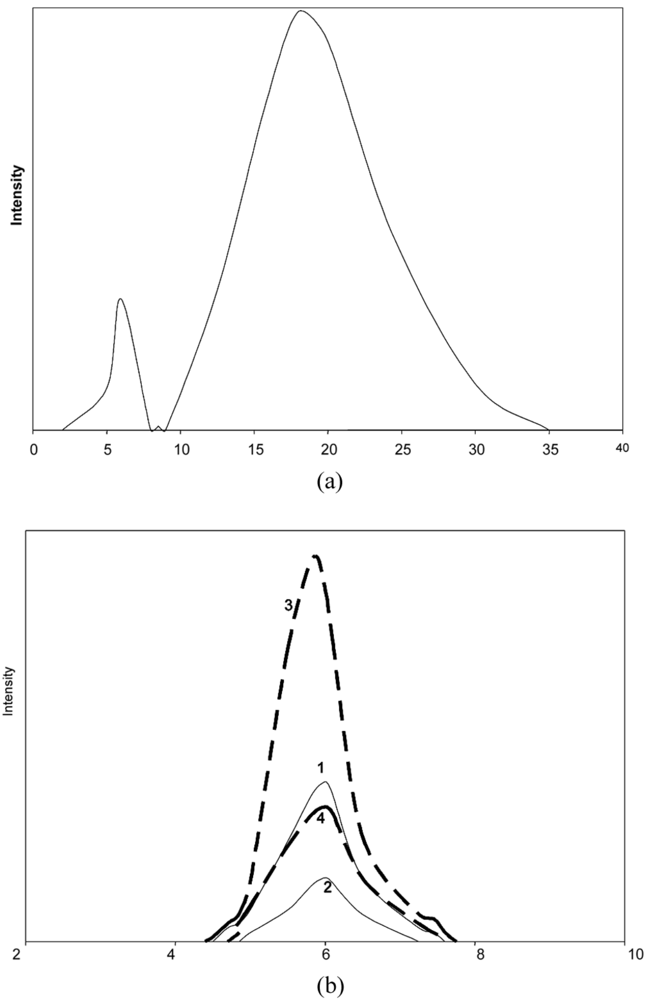


Figure 2. Diffraction patterns for PI films without additives (a,b – 1,2) and added by 2 wt.% APP (b – 3,4) prior to heat aging (a,b – 1,3) and after thermal oxidation (b – 2,4) T = 300°C, 700 h in air.

stabilizing activity. These mechanisms are taken into consideration in the analysis of PSF stabilization during processing:

- phosphorylation or other chemical interactions between SHP and PSF macromolecules or labile and oxidized structures;
- inhibition of high-temperature oxidation radical reactions;
- transition metal admixture deactivation;
- other mechanisms, for example, deactivation of electron-excited states.

Feasibility of the stabilization molecular mechanism was estimated by NMR analysis of pentaerythritol diphophite AO-118 mixtures with oligosulfones (the polymerization degree 5–7), 4,4′-dichlorodiphenylsulfone, or bisphenol a at 280–300°C in vacuum and in air. Under the condition of interaction with phosphite, high content

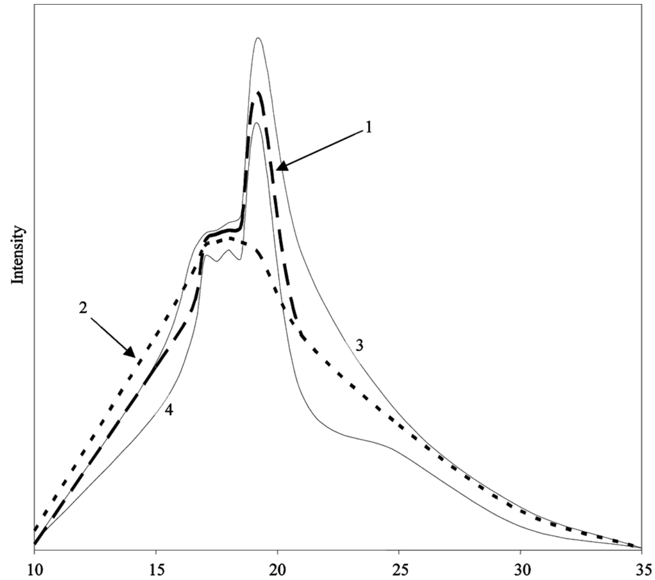
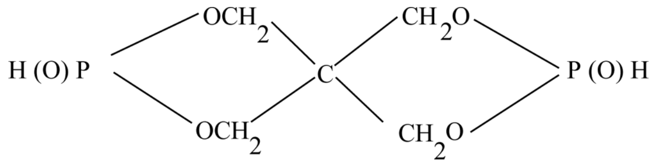


Figure 3. Diffraction pattem for LCP derived from TPA, IPA, p-OBA, and DODP without additives (1, 2) and added by 0.5% lrgafos 126 (3, 4):(1, 3) prior to heat treatment and (2, 4) after thermal processing; T = 300°C; 5 h in air.

of end –OH and –Cl groups in the oligomer and monomers were provided for high resolution observation of phosphorylation by spectral methods. ^{13}C NMR spectra of heat treated mixtures preserve substrate reflexes and their relations that testify about the absence of molecular interactions. On the other hand, heating leads to phosphite decomposition, e.g., hydrolysis to corresponded monophenol and acid pentaerythritol diphosphite, signals from which at 64.5 and 63.4 ppm indicate dominance of tautomeric, four-coordinated shape:



Phosphite additives to preliminarily degraded PSF and further heat treatment do not make the polymer color lighter and, according to IR spectra, have no effect on intensity of absorption bands associated with oxidized structures, for example, carbonyl groups. In other words, phosphorylation, noticeable, in the heat stabilization mechanism in other systems, for example, at PET and PMMA combustion and pyrolysis inhibition [31] or thermal oxidation of synthetic rubbers and vinylchloride polymers [18], is not observed during inhibited high-temperature PSF degradation.

SHP high-temperature stabilization by additives shows signs of radical inhibition: low effective concentrations (optimally, 1–1.5 mmol/kg), the efficiency O_2 pressure (in the absence of O_2 the efficiency is extremely low). SHP decelerates the homolytical process of PSF macromolecule branching during thermal oxidation. Higher efficiency of cyclic SHP, compared with open ones, in the high-temperature oxidation process is, apparently, the general rule, because analogous dependence is displayed at PE high-temperature oxidation (Fig. 4). This may be considered as the model of really radical, high-temperature process.

The increase of SHP effectiveness with hydrolysis probability, shown in experiments with water linking, indicates the significant role of acid esters in inhibition of SHP hydrolysis products. Cyclic SHP of Irgafos 126-type possess chemical shift on ^{31}P nuclei equal to 115–120 ppm, (parts per million) whereas low-effective SHP of tris-(2,4-di-tert-butylphenol)phosphite and common triarylphosphites possess chemical shifts of about 130 ppm, and trialkylphosphites – 137–139 ppm. Since in all cases P–O bond is observed, i.e., at the first glance any change in electronegativity of the partner is absent and changes in SHP chemical shifts (the obvious absence of steric hindrances effect on the chemical shift) are associated with the differences in values of O–P–O bond valent angles in cyclic and open SHP, in agreement with the definition of ^{31}P chemical shift [42]:

$$\Delta\delta = -\mathbf{c}\Delta\chi_{\alpha} + \kappa\Delta\mathbf{n}_{\pi} + \mathbf{A}\Delta\mathbf{Q}$$

where $\Delta\chi_{\alpha}$ is the difference in electronegativity values of P–X-bonds; $\Delta\mathbf{n}_{\pi}$ is the change in π-electron overlapping; $\Delta\mathbf{Q}$ is the change of σ valent angles. The change of valent angles causes changes in configuration of the electron cloud around phosphorus nucleus, i.e., the nucleus screening is changed. Formally, the effect is adequate to the change in electronegativity of partners bonded with phosphorus. Chemical shifts on ^{1}H, ^{13}C and, apparently, ^{31}P nuclei is inversely proportional to electronegativity of the partner nucleus [34], i.e., electronegativity of P is somehow reduced in the phosphite sequence:

cyclic alkylene-aromatic > aromatic > aliphatic.

According to Poling's electronegativity row atoms P, C, and O are equal to 2.1, 2.5, and 3.5. P–O-bond possesses much higher polarity than C–O-bond. That is

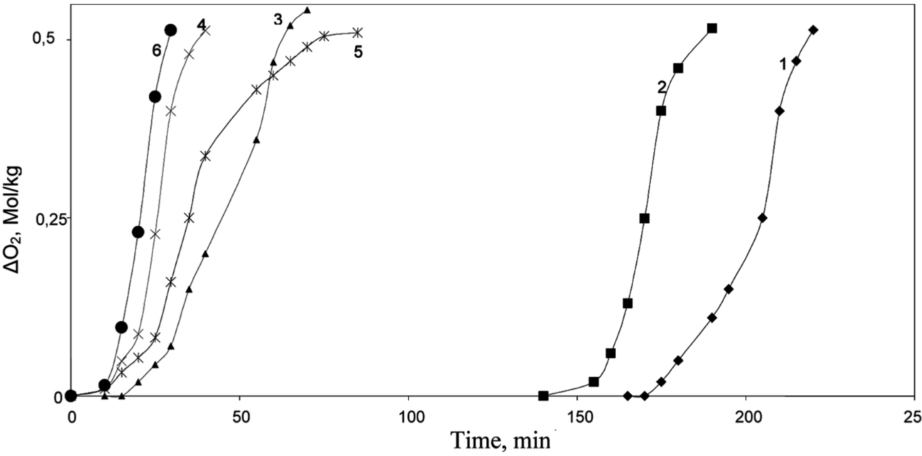


Figure 4. PE oxidation kinetics in the presence of SHP: Irgafos 126 (1, 2), Stafor 11 (3,4), and its acid ester (5, 6) without water absorption (1, 3, 5) and with water absorption (2, 4, 6); T = 200°C, P(0_2) = 399.9 kPa.

why P–O has less hydrolytically stability. Bulky groups of the tert-butyl type in the ortho-position at the ester bond makes steric hindrances to hydrolysis (kinetic mechanism). Changes in valent angles in the six-term steric phosphites reduce polarity of the ester bond and, as a consequence, its hydrolyzing ability (thermodynamic mechanism). For cyclic SHP, both mechanisms of hydrolytic stabilization are realized. Therefore, it is proved experimentally that these phosphites, for example, Irgafos 126 and etc. Are most resistant to hydrolysis [36]. Finally, hydrolysis of open phosphites, including open SHP, leads to H_3PO_3, which is low-effective high-temperature stabilizer. At hydrolysis of cyclic SHP alkylene-ester structure is preserved (NMR data), and the final product (acid cyclic phosphite) is the effective high-temperature stabilizer. This was shown by direct comparison of effectiveness of Stafor 11 (Russian additive) and its acid analogue, specially synthesized for tests. For example, tests performed on reometer – IIRT device at 320°C, showed that Stafor 11 makes PSF color lighter, increasing the light transmittance index by 3–5 units. For PSF acid ester, this index is increased by 10–12 units, although differences in other indices are not so great.

Indirectly, the radical mechanism of SHP stabilizing activity is confirmed by additive elimination of active degrading effect on PSF from the side DMSO. As shown by the strength of C–S-bonds in $(CH_3)_2SO_2$, equal to 264 kJ/mol [37], and higher total reactivity of sulfoxides compared with sulfones [38], DMSO is not heat resistant compound. At low temperature (about 100°C) molecular thermal cis-splitting happens with an olefin formation, although at higher temperatures homolytical C–S-bond break is suggested [38]. Actually, over sixteen main products of DMSO degradation at PSF processing temperature (the ampoule technique) were detected by the mass-spectrometric method. The highest yields are observed for dimethyl disulfide, methyl ethyl sulfide, methyl and ethyl mercaptanes, 3-hydroxypropyl methyl sulfide, methylethoxymethylsulfide, and similar substances, which formation may be explained with respect to alkyl and alkylthio-radical recombination, as well as labile oxygen exchange reactions in semipolar sulfoxide group. As PSF is processed, DMSO residues play the role of an original radical initiator of degradation, and while the SHP addition eliminates this effect.

The idea to deactivate metal admixtures, first of all, iron compounds by SHP additives follows from extremely much higher efficiency of SHP in "impure" samples compared with almost pure ones (Table 1).

If an iron compound (up to 0.005 wt.%) is injected to "pure" PSF, light transmittance will be decreased by 20–30 units, whereas subsequent injection of SHP reduces this effect significantly. On the other hand, PSF color may be stabilized in tests simulating processing of phosphorus-containing transition metal complexes by additives.

Diphenylphosphonic salt additions (cations Co, Cr, Ni, Cu) up to 0.1 wt.% stabilize PSF similar to polyalkane imide, although these effects in PSF are not so high as in case of SHP use. The simplicity of phosphite interaction (*Irgafos 126*, in particular) with transition metal compounds is shown by UV spectra of *Irgafos 126* and model substance (ferrocene), and their mixture chloroform solutions (Fig. 5). At room temperature phosphite and iron-containing model interact, what causes a noticeable deviation of experimental UV-spectrum from calculated (additive) one.

This interaction represents an example of common complex-forming function of phosphorus compounds. With respect to the type of substitutes and coordination degree, phosphorus atom or phosphoryl oxygen is electron donor. The electron lone

Table 1. The dependence of SHP effectiveness on polysulfone purity

Sample	$MFI_{(10\,min,\ 320°C)}$, $g/10_{min}$	$MFI_{10\,min}$/ $MFI_{20\,min}$	Transmittance at $\Lambda = 425\,nm$, %	Moment molecular-mass distribution $M_z\ 10^3$
PSF with $[Fe] = 5 * 10^{-5}$ wt.%	–	–	73.0	99.5
The same sample after IIRT	3.5	1.02	78.0	94.0
The same sample added 0.3 wt.% Irgafos 126	4.3	1.01	73.0	98.0
PSF with $[Fe] = = 5 * 10^{-5}$ wt.%	–	–	60.0	87.0
The same sample after IIRT	3.7	1.5	68.0	58.0
The same sample added 0.3 wt.% Irgafos 126	4.2	1.05	63.0	80.0

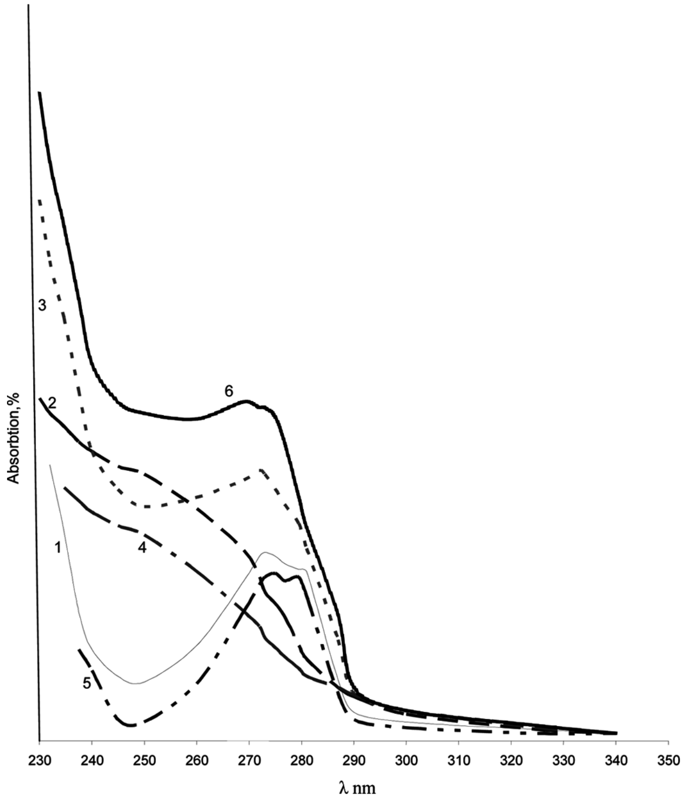


Figure 5. UV-spectra for chloroform solutions of Irgafos 126 (1), ferrocene (2), and their mixture (3), Differential spectra: mixture – Irgafos 126 (4), mixture-ferrocene (5), calculated additive Irgafos 126-ferrocene spectrum (6).

pairs of these atoms are transferred to empty or partly filled α-orbitals of neighboring atom of metal. Phosphorus-metal complexes are strongly bound due to relatively low potentials of phosphorus compound ionization and additional linking of π-electrons because of donor and acceptor (metal) vacant α-orbital overlapping [40].

The donor-acceptor interaction is one of the main mechanisms for metal compound extraction. The extraction ability correlates with the distribution of electron density in extracting agents, including phosphorus-organic compounds [39]. Correlations between effective extraction parameters, defined by thermodynamics of the donor-acceptor bond, and the so-called "effective charge" at phosphorus, by which electron density distribution in molecule is described, and associated parameters of substitute electronegativity was investigated with ^{31}P NMR chemical shift as well. Generally, dependencies of the extraction effective constant (K) logarithm are linear:

$$IgK = A - Bf,$$

where A and B are constants defined by the metal type and parameter f, f is the parameter characterizing electron density, for example, by the sum of electronegativity values of substitutes at phosphorus atom. There are data [39] on effective charges on phosphorus atoms in many phosphorus-containing compounds. Effective charges are determined from X-ray diffraction patterns by the energetic shift of phosphorus absorption range boundaries.

Iron admixtures significantly speed up thermal oxidation of all studied heat-resistant polymers. PCA injection fully eliminates this acceleration. Therefore, PCA stabilizing effect in heat-resistant polymers may be explained by metal admixture binding.

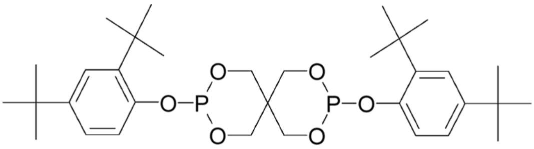
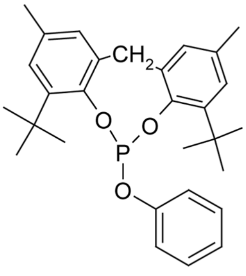
The products of "model + stabilized" system (equimolar mixture of Nphenylphthalimide and AFF) thermal transformation were analyzed with the help of NMR-spectroscopy technique. It is shown that at 250–300°C the model does not transform, and the stabilizer partly degrades forming diphenylamine, phenol, phosphoric acid and its condensation products. All these compounds are not stabilizers of PI, PAI, PPA and other compounds or display much lower stabilizing action than initial AFF. As a consequence, the stabilizing action is defined by either the initial PCA structure or intermediate products of stabilizer transformation. The occurrence of ESR signal (a singlet with $\Delta H = 9.1$ E and $g = 2.0003$) allows a suggestion that stabilizer thermal transformation products are of the radical origin (Table 2).

Emission extinguishing in PI film is observed by fluorescence spectra at 520–530 nm under the effect of AFF additive. The paramagnetism increase as a result of degradation in stabilized samples is much lower than in non-stabilized polymers. This is reproduced both in PI and PAI. Therefore, if electron excitation is considered as the oxidation initiation, endoperoxide formation, thermal activation of the imide structure transfer to the electron-excited state in stabilized samples is hindered.

Thus, the investigation performed allowed the exclusion from consideration unrealizable or weakly realizable PCA effect on heat-resistant polymer cyclization and crosslinking and detection of the most probable stabilization mechanisms – admixture bonding and inhibition of radical-chain oxidation processes.

Optimal PCA concentrations of 2–5 wt.% in PI, PPQ, and PBO and 0.5–1.0 wt.% in PEI, PPA, PSF, and PAI. If one considers that the rate of translational diffusion of low-molecular substances in the rigid structure of heat-resistant polymers is low

Table 2. Chemical names and structures of antioxidants used in article

Trade mark	Chemical structure	Chemical name
Irgafos 126 (Ciba)		Bis-(2,4-di-t-butylphenol) pentaerythritol diphosphite
Stafor 11		O-phenil-O,O-[2,2'methilenbis-(6-t-butyl-4-methilphenil)]-phosphite

and may not provide the additive transport to the oxidation focus, it may be concluded that inhibition is possible only in the additive interaction with macromolecule and changes of its reactivity. Experiments with models did not display phosphorylation, i.e., direct interaction between the additive and aromatic heterocyclic structure. In this case, apparently, a polymer additive complex is formed, which changes the macromolecule reactivity in reaction to oxygen. The complex formation may change the electron state of the whole macromolecule or a large part of it, i.e., change the reactivity of it. Clearly, conjugation blocks are present in the macrochain: PDI in PI and PAI, PPP in PPQ and copolyimide phenylphenoxaline, amide-TPA in PPA, i.e., the products characterizing chain conjugation. Their output at thermal oxidation is decreased by PCA injection, whereas carbon oxides yields are reduced by 1.5–2 times only.

Thus, basing on the totality of experimental data on PCA stabilization one may conclude that the most probable stabilization mechanisms are additive deactivation, inhibition of radical oxidation processes and deactivation of electron-excited states.

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