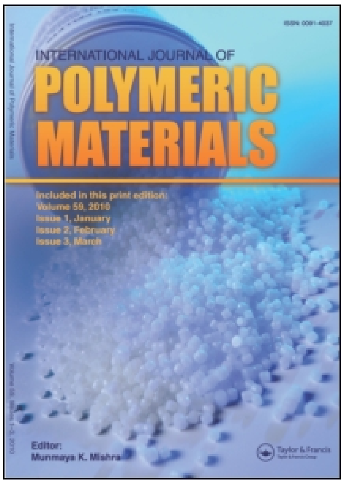

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The Investigation of Oligomeric Azomethyn Dyes' Reactivity during Radical Reactions in Comparison with their Inhibiting Action at Photooxidation of the Cellulose Acetate

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The kinetic data on the effective influence of oligometric dyes-azomethyn compounds (AC) chain conjugation on the polymerization rate of styrol have been obtained. Oligomeric AC reduce radical polymerization rate more than in 10 times in comparison with low-molecular models having —C=N bonds. The reactivity of polyconjugated AC depends on delocalization effeciency of π-electrons along the chain of conjugation.

It has been established that the inhibiting activity of dyes having "carbon-nitrogen" double bonds rises with the increase of polymerization temperature and concentration of oligomeric AC. The results of AC reactivity in radical reactions are correlated in accordance with their light-stabilization in radical processes of photooxidative destruction of cellulose acetate. The use of oligomeric dyes allows for the possibility to control of styrol radical polymerization.

KEY WORDS Azomethyn dyes, photooxidation, cellulose acetate, antioxidants.

INTRODUCTION

A number of articles devoted to the synthesis and use of the oligomeric systems having conjugated azomethyn bonds in the main chain as inhibitors and antioxidants has recently been published.[1,2]

We have earlier shown the possibility to use these compounds as antioxidants for the high-molecular materials.[3,4] However little attention was paid to the study of reactivity of these systems in radical reactions. So it was interesting to examine the reactivity of some low-molecular and oligomeric azomethyns in radical reactions taking the styrol polymerization initiated by benzoyl peroxide as an example.

The object of this article is to examine of reactivity of some low-molecular and oligomeric systems having carbon-nitrogen double bonds in the main chain of conjugation during radical reactions and to compare with AC inhibiting activity at photooxidative destruction of cellulose acetate.

EXPERIMENTAL

Materials

The low-molecular aromatic azomethyns[5] and oligomeric Shiff polybases,[6] whose characteristics and structure are given in Table I, were the objects of investigation. Over 10–15 hours cellulose diacetate was purified from admixtures by three ethanol extractions during 2 hours at the room temperature.

Methods

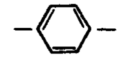
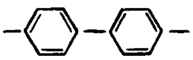
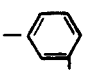
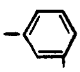
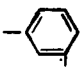
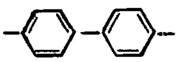
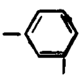
The molecular mass was determined by the isopiestic method.[7]

The content of AC and aminogroups were obtained by methods described by Kaints.[8]

Ultraviolet spectra of AC were taken from the Perkin-Elmer spectrophotometer M-402 at the concentration 5·10^{-5} mol/l in dimethylformamide.

TABLE I

The structure and characteristics of investigated conjugated systems

Product structure	*R*	Mol. weight	Melting point, °C	λ_{max}, nm
PFB—I		1000	145–150	368
BB—I		1200	210–215	348
MFB—I		1680	103–105	310
BMF—II		1400	116–120	332
DBPF—III		284	136	360
DBB—III		360	220	352
DBMF—III		284	128	320

I. $H_2N—R—N[C(C_6H_5)—C(C_6H_5)=N—R—N]_n^{H_2}$.
II. $O=C(C_6H_5)—C(C_6H_5)[N—R—N=C(C_6H_5)—C(C_6H_5)]_n^{O}$.
III. $C_6H_5—CH=N—R—N=CH—C_6H_5$.

The X-ray analysis of structure was done by the apparatus URS-50 with the use of CuKα radiation.

The infrared spectra were taken in KBr tablets at the spectrometer UR-10.

The conjugated system reactivity was studied by dilatometeric method[9] with the dilatometer volume 10 cm^3 with capillary point 0.01 cm^3.

The specific viscosity of the acetone solution of cellulose acetate was determined by a method described in Toroptzeva.[10]

The kinetics of radical processes was studied by dilatomeric method; the fresh distilled dry styrol with addition of 0.2% twice recrystallized benzoyl peroxide in the atmosphere of dry argon was used for this purpose. The temperature of the thermostat was maintained at ±0.01°C.

The measurement of conversion rate depending on temperature in the interval 70–100°C allowed for the possibility to calculate (taking the thermal styrol polymerization rate into consideration) rates and constants of radical polymerization styrol initiation in dependence on the concentration and the structure of the inhibitor (II):

$$V_{in} = \frac{V^2_{pol} \cdot K_e/K_g}{[M]^2}\,; \qquad K_{in} = \frac{V_{in}}{[I]}\,;$$

V_{in}—a rate of initiation; V_{pol}—a rate of polymerization; K_e/K_g—a ratio of chain ending and chain growth polymer constants, $[M]$ and $[I]$—a concentration of the monomer and the initiator, K_{in}—a constant of polymerization initiation.

The system chosen allows us to distinguish the kinetic peculiarities of interaction reactions between inhibitor molecules and radicals of peroxide compound at the action of temperature.

The styrol polymerization was carried out in mass in the atmosphere of inert gas in the presence of benzoyl peroxide, and the temperature of reaction was 60–120°C.

The irradiation of cellulose diacetate films was done with the quatz lamp PRK-2 at a distance of 30 cm.

RESULTS AND DISCUSSION

The experimental results showed that all conjugated systems under study inhibit the radical polymerization. The efficiency of high molecular weight oligomeric azomethyns (PFB, BB, MFB, BMF) (Figure 2, curve 2) is higher than that of the low molecular compounds (FBPF, DBB, DBMF) (Figure 2, curve 1). It is correlated in both cases with the displacement of maximum electron spectrum absorption to the long wave range (Figure 1).

In their chain the polyconjugated systems contain non-divided P-electrons of a nitrogen heteroatom. So the conjugation (delocalization) energy of these molecules is determined not only by the presence of π,π*-conjugation, when the efficiency

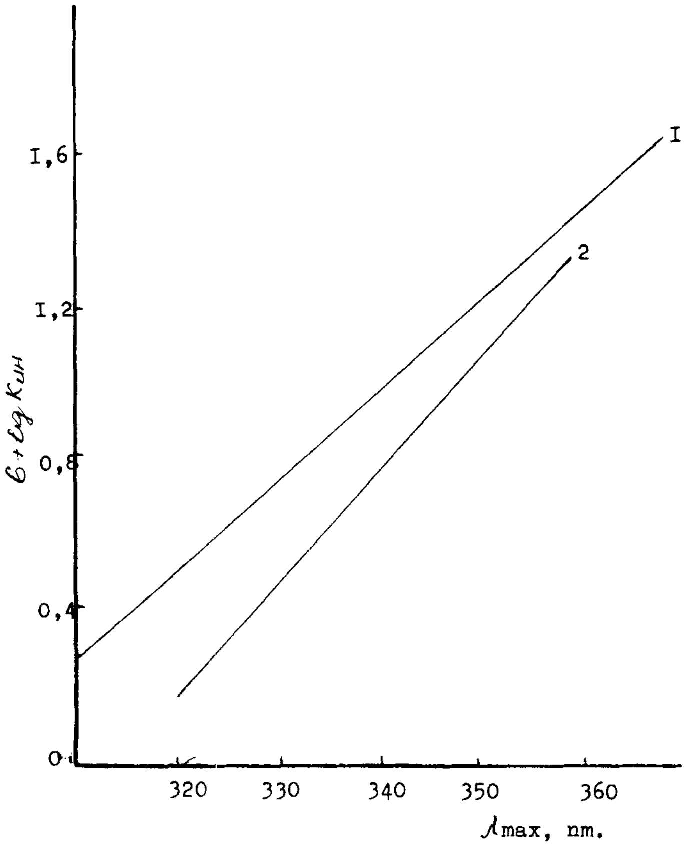


FIGURE 1 The dependence of the rate initiation constant of styrol polymerization on inhibitor conjugation efficiency at 80°C: 1—low molecular azomethyns, [c]—0.01 mol/l; 2—oligomers, [c]—0.001 mol/l.

of delocalization is π = Δ*E*/*N*π, but it also depends on the transition energy of π-electrons from their normal to excited state and it is controlled by the chain conjugation length and the competing effect of p,π-conjugation. Because of this fact the redistribution of electron density occurs and the efficiency of conjugation is reduced. And unlike with polyenes we see the gipsochromic shifting with the growth of chain conjugation length.[6] Such "blue" shifting in ultraviolet spectra of low molecular and oligomeric azomethyns leads to the reduction of an initiation constant of the styrol radical polymerization and consequently to the growth of inhibiting activity of a AC (Figure 1).

It is worth mentioning that the efficiency of oligomeric stabilizing agents is 10 times higher than for their low molecular analogs. The polyconjugated oligomers also have high thermal stability; according to TGA the mass loss is 5% in PFB; 18% MFB; 4% BMF at 300°C and 8% in BB at 400°C. Such high thermostability of stabilizing agents is explained by the presence of conjugation, its efficiency and the nature of AC end groups; the latter confirms that thermal destruction of polyconjugated molecules begins at the chain ends.

In the radical processes the inhibiting efficiency of polyconjugated oligomers (PCO) is caused by azomethyn bonds and by primary amine end groups which are intensified by "the system of effective conjugation." The PCO characteristics depend on delocalization efficiency of π-electrons along the conjugation chain which is determined by the overlaping of π-electrons orbitals. Such overlapping is maximized at the coplanarity of distribution of double bonds taking part in conjugation and is reduced at where end substitutes, functional groups, intermolecular interaction are taken out of the coplanar system and heteroatoms are put in. These conformities were confirmed by the study of the rate dependence of inhibiting styrol polymerization on AC structure (Figure 2).

It should be mentioned that the inhibiting activity rises with temperature increase, a fact peculiar to polyconjugated systems.[2]

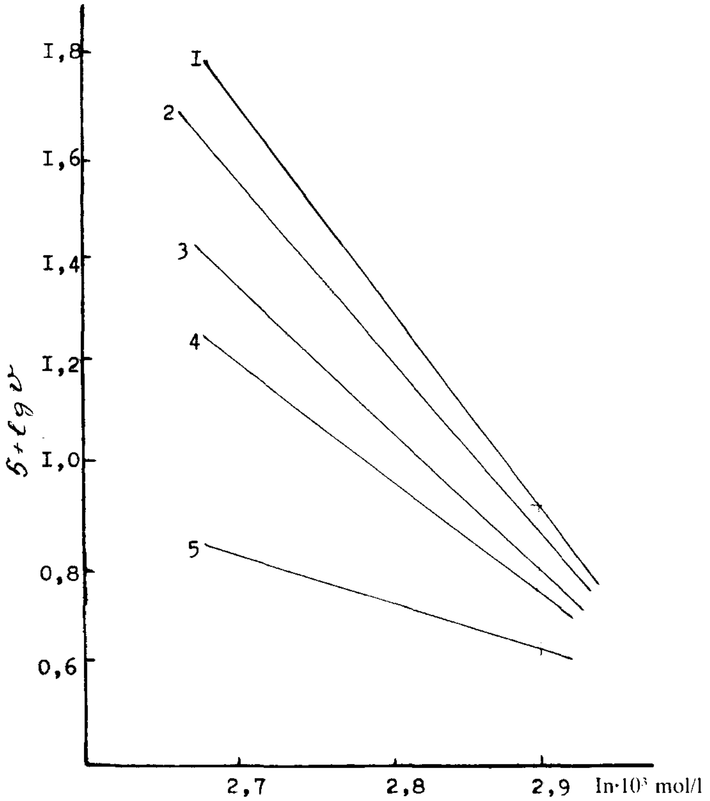


FIGURE 2 The dependence of inhibited styrol polymerization rate on the inhibitor structure: 1—without inhibitor; 2—BMF; 3—PFB; 4—BB; 5—MFB; [c]—0.0005 mol/l.

The higher MFB inhibiting activity is probably connected with better configuration lability of the oligomeric molecule in radical reactions.

It has been assumed that inhibiting activity of polyenes is determined by the length of the conjugation chain and by presence of paramagnetic particles[14] and rises with the increase of their content. The magnetic fields of paramagnetic particles make the transition of molecules into excited state easier and raise their reactivity with respect to free radicals. The stable complexes are formed between paramagnetic particles and radicals. However this assumption is not essential with polyshiff bases which are paramagnetic and give a narrow singlet with g + 2.0025 ± 0.0005 and δH from 10 to 20 ersted, traits peculiar to semiconducting polymers. But their efficiency is radical reactions decreases in the order MFB > BB > PFB. Since their inhibiting action on radical reactions rises with temperature (Figure 2) they are suited for use as thermal stabilizing agents.[3]

Sometimes when thermal oxidative destruction of high molecular compounds is stabilized, we have for some stabilizing agents the extreme dependence of the inhibitor efficiency at the fields of high concentrations which connected with the initiating action of inhibitor radicals. We have seen such a phenomenon at the stabilization of polyethylene low density with MFB when the period of induction begins to fall at polymer concentration exceeding 0.01 mol/kg.[4]

The study of inhibiting efficiency of PCO on radical processes showed that the rate of styrol polymerization reaction goes down as the concentration increase from 0.0003 to 0.001 mol/l and depends also on structural peculiaries and chain conjugation efficiency of the oligomeric stabilizing agent (Figure 3).

In other articles (15–16) it was shown that photodestruction of cellulose acetate is accompanied by free radical formation. So it was interesting to compare characteristics of oligomeric reactivity with their light protective action at ultraviolet irradiation of cellulose diacetate. These characteristics are given in Table II.

Table II shows that according to their inhibiting activity it is possible to put AC in the order MFB > BB > PFB > DBPF that correlates with AC order when we have inhibiting styrol polymerization.

Thus, the oligomers with conjugated azomethyn bonds are more effective as radical inhibitors than their low-molecular analogous compounds. Their reactivity depends on chain conjugation length and efficiency, temperature of reaction, and oligomeric concentration.

TABLE II

Specific viscosity preservation of 0.5% acetone solutions of cellulose diacetate having 2 percent AC in weight before and after irradiation by Hg-quartz lamp over 10 hours

Cellulose diacetate film, containing	Preservation specific viscosity, %
Initial	28.9
DBPF	33.0
PFB	84.0
BB	89.0
MFB	9.30

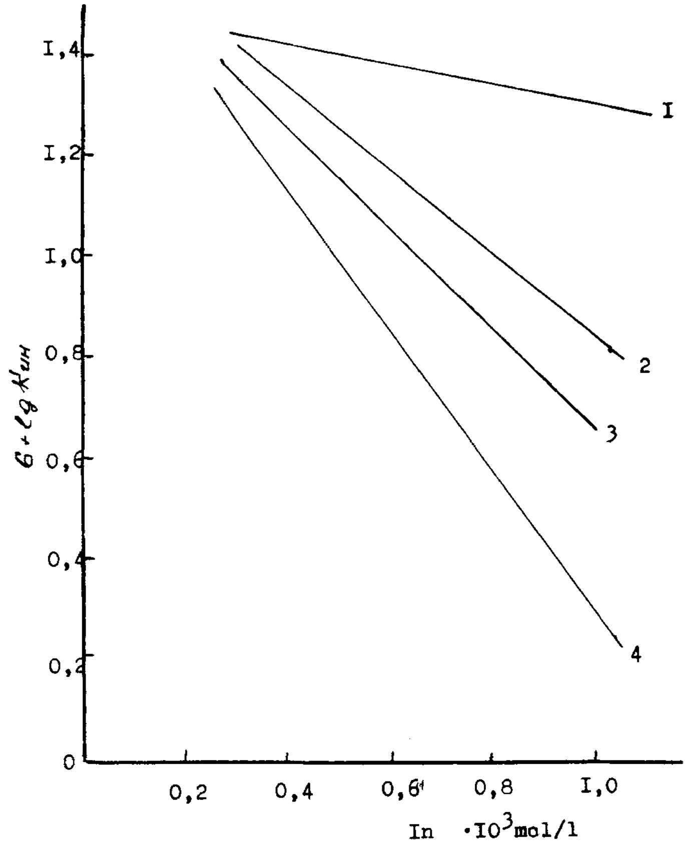


FIGURE 3 The influence of the concentration of PCO on the rate constant of inhibited polymerization of the styrene at 80°C: 1—BMF; 2—PFB; 3—BB; 4—MFB.

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