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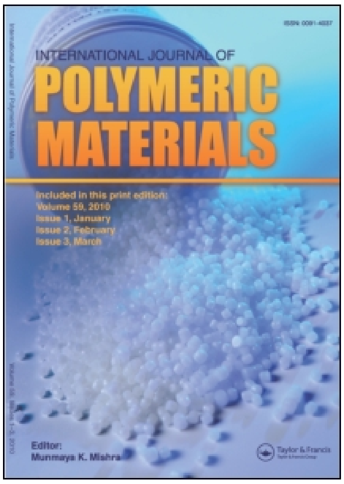

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Interaction of Polyamide-6 with Mixtures of Oxyaromatic Compounds

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Interaction of polyamide-6 with the mixtures of oxyaromatic compounds introduced in the amorphous regions of polymer from aqueous solutions is shown to be controlled by the competing complexation reactions between the mixture components with polymer macromolecules. The principal contribution to binding with polymer matrix is provided by the component, which is able to produce a cooperative set of intermolecular hydrogen bonds with polyamide-6 macrochains. The development of the cooperative intermolecular bonds between the molecules of oxyaromatic compounds and polymer macromolecules is discussed in terms of structural inhomogeneity of amorphous phase of polyamide-6: co-existence of structural sublevels with different packing densities.

Keywords: PA-6; oxyaromatic compounds; interaction; structure

INTRODUCTION

In previous papers [1-3] we showed that, in some cases, introduction of Oxyaromatic Compounds (OACs) to PA-6 from their aqueous solutions is accompanied by the distribution of these low-molecular-mass agents in polymer matrix between Reversibly Bound (RB) and Irreversibly Bound (IB) forms. As compared with IB form, the RB form of OAC may be easily removed from polymer by treatment of PA-6 with OAC in pure solvent (water). The similar distribution of

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low-molecular-mass compounds between IB and RB forms was observed for Br_2 in poly(acrylonitrile) [4] and dioxydine in copolymer of *N*-vinylpyrrolidone with methyl methacrylate [5].

In [6, 7], the development of IB form of OAC in PA-6 was discussed in terms of complexation between molecules of OACs and polymer macromolecules taking into consideration structural inhomogeneity of amorphous regions of PA-6, that is, co-existence of noncrystalline structural levels with different packing densities and ordering. Let us note that structural inhomogeneity of amorphous phase of semicrystalline polymers, in particular, polyamides, was widely discussed in literature (for example, in [8 – 10]).

The formation of IB form of OAC was shown to be controlled by the development of a cooperative set of hydrogen bonds between phenol hydroxyls of OACs and amide groups of polymer. Depending on chemical structure of OAC molecules, IB portion of OAC may be produced both in the loosely packed structural sublevels and in the densely packed structural sublevels or may not be formed.

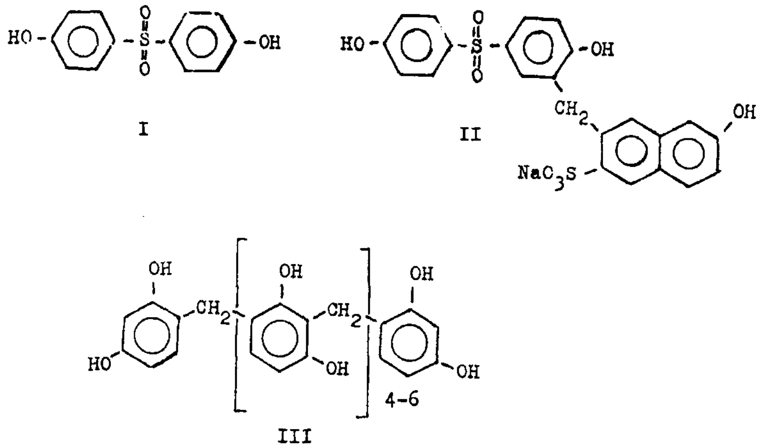
The aim of the present work was to investigate the distribution of OACs between IB and RB forms during the introduction of mixtures of these low-molecular-mass agents into PA-6.

EXPERIMENTAL

We studied the commercial isotropic films of PA-6 (trademark PK-4, Russia) with a thickness of 0.1 mm. Before testing, the samples were treated in boiling water for 3 h. After that, they were dried over P_2O_5 until constant mass was attained.

As OACs we used dioxydiphenylsulfone (I), synthetic tanning agent (II), which was prepared by condensation of sulfonated β-naphthol and dioxydiphenylsulfone with formaldehyde, and resorcinol-formaldehyde novolac (III). The low-molecular-mass compounds were purified using dialysis. The purity of OACs was controlled by IR-spectroscopy.

The films of PA-6 were treated at 100°C in aqueous solutions of OACs with concentrations: 0.0125 and 0.025 (OAC I), 0.0125 and 0.025 (OAC II), 0.025 (OAC III) mol/l, as well as in aqueous solutions of mixtures of OAC II with OAC I and OAC III with OAC I until



I

II

III

SCHEME I

equilibrium sorption of OACs by polymer was attained. Molar fraction of OAC III in its mixture with OAC I was 0.5 (mixture of 0.025 mol of OAC III with 0.025 mol OAC I was dissolved in 1 l of water). Molar fractions of OAC II in its mixture with OAC I were 0.33 (mixture of 0.0125 mol OAC I with 0.025 mol OAC I was dissolved in 1 l of water), 0.5 (mixture of 0.025 mol OAC I with 0.025 mol OAC I with 0.025 mol OAC I was dissolved in 1 l of water), and 0.66 (mixture of 0.025 mol OAC I with 0.0125 mol OAC I was dissolved in 1 l of water). After the treatment of PA-6 films in aqueous solutions of OACs, the samples were dried over P_2O_5 until constant mass was attained. Concentration of OACs (or their mixtures) sorbed by the polymer samples was estimated gravimetrically.

To obtain quantitative estimates of OACs introduced into PA-6 films between RB and IB forms, the PA-6 films with OACs were treated in boiling water until equilibrium desorption of OACs from polymer was attained. The IB form of OAC was defined as the fraction of OAC that cannot be removed from PA-6 samples by their treatment in boiling water.

The estimation of the composition of mixture of OACs, which may be desorbed from PA-6 samples after their treatment in aqueous solutions of mixtures of OAC I and OAC II, was carried out as follows. The water, in which PA-6 films containing OACs were treated, was evaporated using water bath. After that, the pellet of dry residue with KBr was prepared. IR-spectra of this pellet were taken using a Specord M-80 instrument (Germany). The content of OAC II was estimated from the ratios of intensities of 840, 900, and 1030 cm^{-1} bands according to [11].

RESULTS AND DISCUSSION

Figure 1 shows the kinetic curves describing desorption of OACs from PA-6 films. This experimental evidence suggests that, for individual

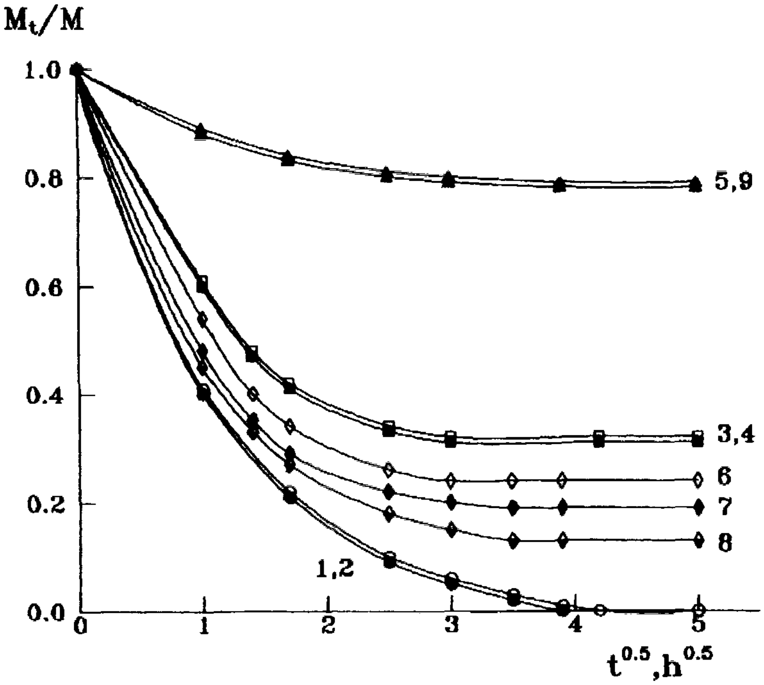


FIGURE 1 Kinetic curves of desorption of OACs from PA-6. M_t - content of OAC in PA-6 after desorption for a time t, M - equilibrium content of OACs in PA-6 treated with aqueous solutions of OAC I with concentrations 0.0125 (1) and 0.025 (2), OAC II with concentrations 0.0125 (3) and 0.025 (4), OAC III with concentration 0.025 (5) mol/l, mixtures of OAC II with OAC I (molar fraction of OAC II was 0.66 (6), 0.5 (7), and 0.33 (8)), and mixture of OAC III with OAC I (molar fraction of OAC III was 0.5 (9)).

OACs I–III, the formation of IB portion is observed for OACs II (curves 3 and 4) and III (curve 5). The fractional contents of IB form in the total content of these OACs in polymer are 0.32 ± 0.02 and 0.78 ± 0.02, respectively. OAC I is not able to produce in PA-6 IB form and may be completely desorbed from polymer (curves 1 and 2).

Desorption of OACs from PA-6 films treated in aqueous solutions of mixture of OAC II with OAC I and mixture of OAC III with OAC I (curves 6–9) evidences that, in all cases, the formation of IB form is observed. The above results on desorption of individual OACs from polymer allow one to conclude that only OACs II and III are able to produce IB form during the sorption of their mixtures with OAC I.

After the treatment of PA-6 films in aqueous solution of mixture of OAC III with OAC I, the fractional content of IB form in polymer matrix is equal to that as observed after the treatment of PA-6 films with aqueous solution of OAC III (curves 5 and 9). Hence, the presence of OAC I in mixture has no effect on the distribution of OAC III between IB and RB forms in the amorphous regions of PA-6.

In the case of PA-6 films treated with aqueous solutions of mixtures of OAC II with OAC I, as the concentration of OAC I in mixture increases, fractional content of IB form of OAC II decreases (curves 6–8). To obtain a detailed information concerning the effect of OAC I on the distribution of OAC II in PA-6 between the IB and RB forms, the fractional content of RB form of OAC II in polymer matrix was estimated.

To this end, the composition of mixture of OAC II and OAC I desorbed from PA-6 was examined using IR-spectroscopy. Figure 2 shows the corresponding IR-spectra of OAC I and OAC II (curves 1 and 2, respectively), as well as the IR-spectra of low-molecular-mass compounds desorbed from PA-6 films treated with aqueous solutions of mixtures of OAC II with OAC I (curves 3–5). OAC II may be identified from the 900 and 1030 cm^{-1} bands. These absorption IR bands are associated with $R\text{-}SO_2OH$ groups or related salts [12]. With increasing the concentration of OAC II in aqueous solutions of OAC II with OAC I, the intensities of 900 and 1030 cm^{-1} bands increase. This experimental evidence allows one to conclude that the concentration of OAC II in the mixtures of OAC II with OAC I desorbed from PA-6 increases. The concentration of OAC II in mixture of OAC II with OAC I desorbed from PA-6, that is, the content of RB form of

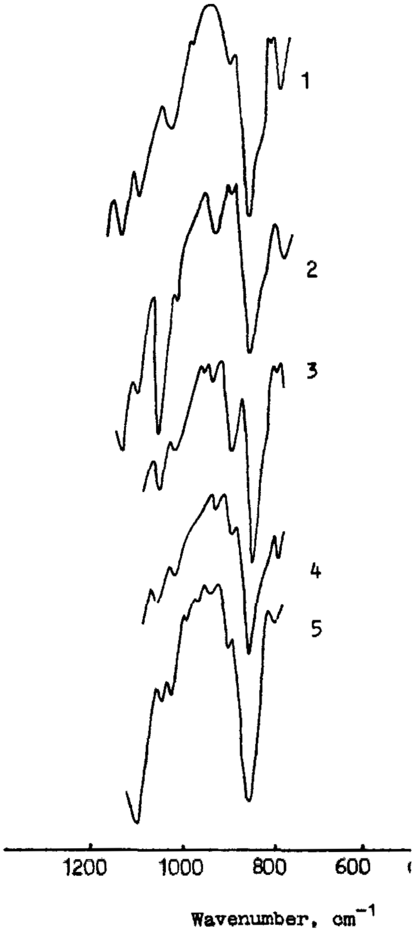


FIGURE 2 The absorption IR-spectra of OAC I (1) and OAC II (2) as well as of residues desorbed from PA-6 films after their treatment with aqueous solutions of mixtures of OAC II with OAC I. Molar fractions of OAC II in mixture with OAC I were 0.66 (3), 0.5 (4), and 0.33 (5).

OAC II in polymer, may be estimated from the ratio between the intensities of 900 and 1030 cm^{-1} bands and intensity of 840 cm^{-1} band. Let us note that the latter band is characteristic of both OAC II and OAC I. Molar fractions of OAC II as well as its IB and RB forms are presented in Table I.

TABLE I Concentration of OAC II and fractional content of its IB and RB forms in mixture with OAC I in PA-6 as a function of concentration of OAC II in mixture with OAC I in aqueous solutions

Molar fraction of OAC II in mixture with OAC I in aqueous solution	*Molar fraction of OAC II in mixture with OAC I in polymer matrix*			*[IB]/([RB]+[IB])*
	total	*IB form*	*RB form*	
1.0	1.0	0.32	0.68	0.32
0.66	0.23	0.14	0.09	0.61
0.5	0.17	0.12	0.05	0.71
0.33	0.12	0.08	0.04	0.67
0	0	0	0	

This evidence suggests that, at first, the dependence of molar fraction of OAC II in its mixture with OAC I in polymer on molar fraction of OAC II in its mixture with OAC I in aqueous solutions does not show additivity (Fig. 3, curve 1). This implies that the preferential sorption of OAC I from the aqueous solutions of mixtures of OAC I with OAC II by PA-6 takes place. Secondly, OAC II introduced to PA-6 from aqueous solutions of mixtures of OAC II with OAC I primarily exists in polymer in its IB form. The fractional content of IB OAC II, with respect to the total content of OAC II in polymer, [IB]/([RB]+[IB]) is 0.66 ± 0.05, independently of the concentration of OAC II in aqueous solutions of its mixture with OAC I. Let us note that, for sorption of individual OAC II by polymer, the corresponding value is 0.32 ± 0.02. Deviation of dependence of molar fraction of IB OAC II in mixture of OAC II with OAC I in polymer on molar fraction of OAC II in its mixture with OAC I in solution from additivity is not noticeable (Fig. 3, curve 2).

The development of IB form of OAC in PA-6 is controlled by the specific features of complexation of OAC molecules with polyamide macromolecules in the amorphous phase of polymer [6, 7]. These features are associated with structural inhomogeneity of amorphous phase, that is, co-existence of, at least, two different noncrystalline levels with different packing densities. The development of IB OAC is controlled by the complexation between OAC and PA-6, and the as-formed complex is stable to action of solvent (in this case, water). The development of stable complexes between low-molecular-mass compounds and macromolecules is observed when cooperativity of a

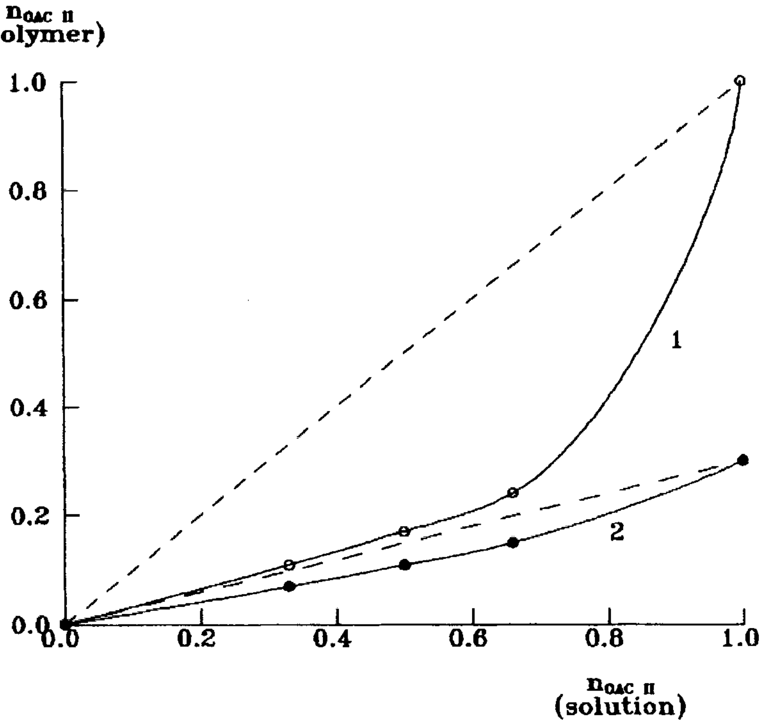


FIGURE 3 Molar fraction of OAC II in mixture with OAC I in PA-6 (1) and molar fraction of IB OAC II in mixture of OAC II with OAC I in PA-6 (2) versus molar fraction of OAC II in mixture with OAC I in aqueous solution. Dashed lines correspond to additivity.

set of intermolecular bonds takes place, and joint dense packing of the molecules of the reacting compounds is realized. The fulfillment of these conditions in the amorphous phase of PA-6 is decided by the chemical structure of molecules of low-molecular-mass compounds (molecular size and number of complexing groups) and local packing of macromolecules.

In the case of OAC II, cooperative interaction with PA-6 macromolecules, that is, the development of IB form, takes place only in the densely packed regions of the amorphous phase of PA-6. In the loosely packed regions, OAC II exists in its RB form and may be easily removed from polymer. When passing to OAC III, with increasing the molecular size and number of complexing hydroxyl groups, the development of IB form also in the loosely packed regions of the amorphous phase of PA-6 takes place. For OAC I, the development of only RB form suggests that no cooperative interaction of the molecules of this low-molecular-mass compound with PA-6 macromolecules is observed in the whole amorphous phase.

When the mixtures of OACs are sorbed by PA-6, both in loosely and densely packed structural regions there is a competition between the components of mixture in complexation with PA-6 macromolecules. In this case, the component of mixture that is able to produce a cooperative set of intermolecular bonds with PA-6 macromolecules has more advantages in binding with polymer [13, 14]. In the case of the mixture of OAC I with OAC III, only the latter is capable producing cooperative interaction with polymer macrochains in amorphous regions of PA-6 [7]. In connection with this, preferential binding of OAC III with PA-6 is observed. Let us note that OAC I seems to have no effect on the complexation between OAC III and PA-6 macromolecules as well as on the distribution of OAC III between IB and RB forms (Fig. 1, curves 5 and 9).

In the case of mixtures of OAC I with OAC II, the latter component is able to produce a cooperative interaction with PA-6 macromolecules but only in the densely packed structural sublevels of the amorphous phase of polymer [7]. Within these structural sublevels, as evidenced by slight deviation of curve 2 (Fig. 3) from additivity the preferential binding of OAC II by PA-6 is observed.

Within the loosely packed structural regions in the amorphous phase of PA-6, for both OAC I and OAC II no development of cooperative interaction with polymer macromolecules is observed. Within these structural sublevels, these low-molecular-mass compounds exist in their RB form. Nevertheless, as evidenced by rather low molar fraction of RB OAC II (Tab. I) the loosely packed regions are enriched with OAC I. This evidence may be rationalized by the fact that molecules of OAC II involve ionogenic SO_3Na groups, which as compared with OAC I provide a better affinity of this low-molecular-mass compound toward water. As a result, the sorption of low-molecular-mass compounds from aqueous solutions of mixtures of OAC II with OAC I is accompanied by the enrichment of the loosely packed structural regions with OAC I.

Hence, the sorption of mixtures of OAC I with OAC II by PA-6 is accompanied by the distribution of the components of mixtures between different structural regions in the amorphous phase of polymer. Within the loosely packed regions, the preferential binding of OAC I is observed. On contrary, OAC II is primarily sorbed by the densely packed regions. Eventually, as evidenced by the deviation of curve 1 (Fig. 3) from additivity amorphous phase of PA-6 is enriched by OAC I.

CONCLUSION

Sorption of mixtures of OACs from their aqueous solutions is associated with the competing in complexation reactions between the mixture components with polymer macromolecules. The component of mixture that is able to produce a cooperative set of intermolecular bonds with PA-6 macrochains is predominantly bound by polymer. The development of the cooperative set of intermolecular bonds is controlled by the chemical structure of molecules of OAC (molecular size and number of complexing groups) and local packing of macromolecules. These factors are responsible for the enrichment of structural regions of amorphous phase of PA-6 with different packing densities with the certain component of mixture.

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