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Effect of Metal Diketonates on Thermooxidative Destruction of Copolymers of Methyl Methacrylates with Methacrylic Acid

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Abstract — Titanium and erbium diketonate additives enhance resistance of films of copolymers of methyl methacrylates with methacrylic acid to thermooxidative destruction.

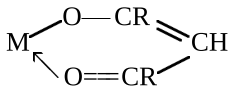
There are many ways to modify traditional polymers, one of which involving introduction of metal atoms into the macromolecules. Metal polymers can be used for production of composite materials with new physical mechanical and service characteristics [1].

In the present work we introduced metal atoms into a copolymer of methyl methacrylate with methacrylic acid by adding metal diketonates to polymer solutions with subsequent removal of the solvent and heating of the resulting films in an inert atmosphere. We expected that upon heating metal salts would replace the methoxy group in methyl methacrylate units, as in the reactions of cobalt acetylacetonates with poly(methyl methacrylate) [2]. Successive cleavage of the diketonate groups attached to the same metal atom would result in cross linking of neighboring macromolecules, thus rendering the polymer less soluble.

We prepared films of the copolymer of methyl methacrylate with 20 mol% of methacrylic acid with erbium trisdiketonate $Er[OC(Ph)=CC(O)CF_3]_3$ (**I**) and titanium dichlorobisdiketonate $Cl_2Ti[OC(t\text{-}Bu)=CC(O)(t\text{-}Bu)]_2$ (**II**) additives (1 mol/kg each). The IR spectra of the copolymer with additives **I** and **II**, like those of diketonates **I** and **II**, contain a band at 1620 and 1500 cm^{-1}, respectively, assignable to the C=O group in ketonate complex **A**.

After the films had been heated in ampules in argon for 1 h at 200°C and then for 1 h at 250°C, their spectra changed considerably. In the spectrum of the copolymer with additive **I**, the ketonate C=O absorption band at 1620 cm^{-1} attenuated 3 times, and the respective band of the copolymer with additive **II** at 1500 cm^{-1} disappeared. The polymer became insoluble, and its glass transition temperature increased from 140 to 275°C.

The resulting data suggest that metal diketonates react with the copolymer ester groups. As a result, metal atom should be incorporated into the copolymer. Probably, on heating of the polymer with erbium trisdiketonate only two of the three diketonate groups of the latter are involved in reaction to form a bridge between macromolecules. The remaining diketonate complex does not react and gives the band of reduced intensity at 1620 cm^{-1}. With titanium dichlorobisdiketonate, both diketonate groups cleave from the titanium atom, and the absorption band of titanium ketonate complexes at 1500 cm^{-1} disappears completely. Simultaneously, in the spectra of heated films we observe appearance of new bands assignable to six-membered anhydride rings whose formation by the reaction of the ester groups of methyl methacrylate units with the carboxy groups of methacrylic acid units, initiated above 170°C, has been revealed by Kalinushkin and Ryabov [3].



A

Recently [4] we obtained evidence for the formation of six-membered anhydride rings in initial stages of thermooxidative destruction of copolymers of methyl methacrylate with methacrylic acid at 277°C [4].

The formation of anhydride rings on thermolysis of poly(methyl methacrylate) in the presence of zinc chloride at 300°C in a vacuum has been reported by Ruban and Zaikov [2], and this mechanism is not ruled out in the case of heating of the copolymer with additive **II**.

We performed a thermogravimetric analysis at 304°C of samples of the copolymer of methyl

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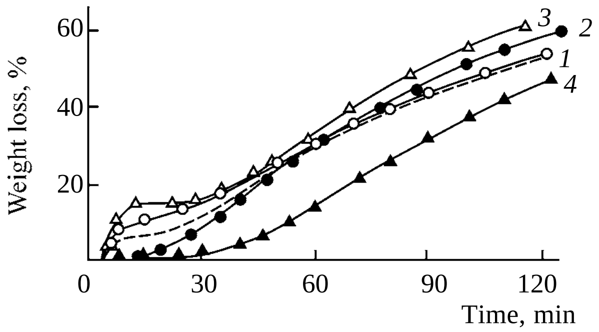

Fig. 1. Weight loss curves for thermooxidative destruction of the copolymer of methyl methacrylate with 20 mol% of methacrylic acid with erbium trisdiketonate (**I**) additives (mol/kg): (*1, 2*) 1.1×10^{-2} and (*3, 4*) 8.5×10^{-2}. (*1, 3*) Unheated and (*2, 4*) heated films. (Dotted line) Weight loss of unheated copolymer without additives.

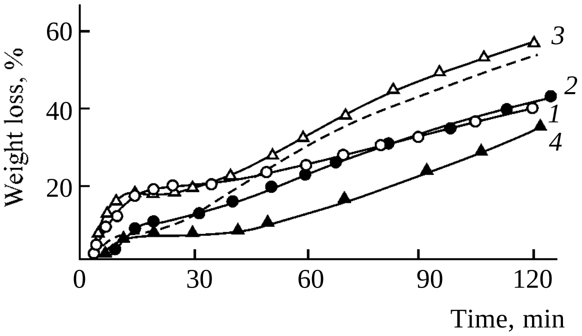

Fig. 2. Weight loss curves for thermooxidative destruction of the copolymer of methyl methacrylate with 20 mol% of methacrylic acid with titanium dichlorobisdiketonate (**II**) additives (mol/kg): (*1, 2*) 0.9×10^{-2} and (*3, 4*) 8.7×10^{-2}. (*1, 3*) Unheated and (*2, 4*) heated films. (Dotted line) Weight loss of unheated copolymer without additives.

methacrylate with 20 mol% of methacrylic acid with varied concentrations of additives **I** and **II**. The samples were both unheated or heated in an inert atmosphere before experiments.

Figure 1 shows the weight loss curves for the copolymer with additive **I**. Unheated films decompose with an induction period of up to 30 min, and the decomposition rate is slightly increased at increased of the additive concentrations. Preheated films with a higher additive content decomposes slower than those with a lower additive concentration. With unheated samples, intensive decomposition of the additives themselves takes place in initial stages (Fig. 1, curves *1* and *3*). Therefore, at τ = 0–10 min, the weight loss of up to 15% is observed, after which the sample weight remains unchanged up to τ = 30 min and then the decomposition rate gradually increases.

Heated samples (Fig. 1, curves *2* and *4*) exhibit no weight loss at τ = 0–15 min. After the induction period, the sample with a higher additive concentration (Fig. 1, curve *4*) decomposes slower than that with a lower additive concentration (Fig. 1, curve *3*); therewith, the heated sample with a lower additive concentration decomposes faster that the unheated sample with the same concentration of additive **I**.

Similar effects are observed with films with additive **II** (Fig. 2). However, heated samples (Fig. 2, curves *2* and *4*) at τ from 0 to 10–12 min show a marked weight loss (up to 10%). It can be assumed that the Cl atoms attached to Ti react with the ester groups of methyl methacrylate units, forming chlorine-containing products analogous to those formed by thermolysis of poly(methyl methacrylate) in the presence of chromium chloride [2].

Probably, the reduced rate of decomposition of heated samples is associated with an effect of the anhydride rings formed in the films at the preheating stage. However, the observation of different decomposition rate–additive concentration dependences for unheated and heated samples suggests that metal atoms are covalently bound to macromolecules and thus affect the thermal oxidation. Evidence for the cross linking of macromolecules, resulting from polymer–additive reactions, comes from the fact that heated samples are insoluble.

EXPERIMENTAL

The IR spectra were measured on a UR-20 spectrometer for films.

The synthesis of the copolymer has been described in [4]. Erbium and titanium diketonates were supplied by V.K. Khamylov. The films were prepared from acetone solutions and dried in a vacuum at 60–80°C. Film thickness ~100 μm.

Thermogravimetry was performed at 304 ± 1°C and an oxygen pressure of 200 mm.

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