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Thermooxidative Degradation of Poly(methyl methacrylates) Containing β-Diketonate Fragments

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Abstract—Thermooxidative degradation of poly(methyl methacrylates) containing in the chain cobalt, copper, and nickel 3-allylpentane-2,4-dionate residues was studied. The increase in the initial degradation temperature is associated with a change in the termination mechanism, decrease in the number of double bonds, and increase in the number of branchings. The increase in the final degradation temperature is associated with the formation of anhydride rings and chain branching, and is always proportional of the metal content of the polymer.

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Production of polymers of enhanced stability is one of the major problems of polymer science. There are two principal approaches to stability enhancement: synthesis of polymers of improved quality and stabilization of polymers with special additives. Thermal stability of polymers depends on the strength of chemical bonds in the macromolecules. Intermolecular interactions responsible for mechanical and other properties of polymers are not directly related to their thermal stability, but the rate of thermooxidative degradation depends on the rate of oxygen diffusion into the polymer. Therefore, thicker packed polymers possess a higher thermal stability [1].

Thermooxidative degradation has a radical mechanism and involves cross-linking along with cleavage of the macromolecules. Poly(methyl methacrylate) degrades by the depolymerization mechanism to form more than 90% of the monomer. Depolymerization initially involves cleavage of the weakest bonds in benzoyl peroxide and its fragments, which are present in the system. As the depolymerization degree increases to 8%, the activation energy of the process increases [2].

Polymers are stabilized by antioxidants and other stabilizers. The most common antioxidants are binary systems comprising an oxidation inhibitor and a reducer for hydroperoxide groups which are intermediate products of thermooxidative degradation [3]. The most potent inhibitors of polyolefin thermodegradation are aromatic amines and alkyl-substituted phenols, nitro compounds, stable radicals, etc. Over the past years great interest has been attached to metal compounds as polymer stabilizers [4]. Influence of ferrocene on the molecular weight and thermal stability of poly(methyl methacrylate) has been explored [5]. Numerous works have been devoted to the stabilizing action of fullerenes [6, 7]. Some effort has been on the stabilizing effects of metal β-diketonates [8-11]. However, there are certain factors that adversely affect stabilization efficiency when a polymer and a stabilizer are mixed mechanically, such as nonuniform antioxidant distribution over polymer bulk, presence of an interface, and antioxidant washing-out on exploitation. Therefore, of interest is to introduce into a polymer, already during its synthesis, stabilizing groups that are chemically bound with the macromolecule.

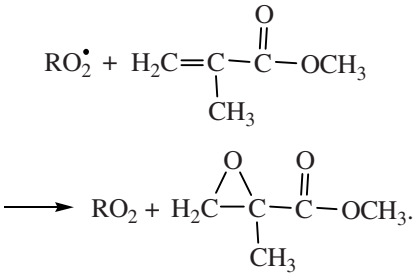
Previously we suggested transition metal vinyl β-diketonates as initiators of radical polymerization. They enter a macromolecule due to their double bond [12]. We found that β-diketonates act as polymerization inhibitors [13]. In this connection we expected that the inhibiting effect of β-diketonate fragments would reveal itself in thermooxidative degradation, too.

The aim of the present work was to study the thermooxidative degradation of poly(methyl metha-

crylate) samples obtained with cobalt(II), copper(II), and nickel(II) 3-allylpentane-2,4-dionate initiators (compounds **I–III**, respectively) under various conditions.

Dependences of the initial (T_{init}) and final (T_{fin}) degradation temperatures on the conditions of synthesis of poly(methyl methacrylate) samples were obtained. Table 1 shows the dependence of T_{init} and T_{fin} on the con-centration of initiator **I** and polymerization temperature.

It is known that poly(methyl methacrylate) thermolizes by more than 90%, and the second most abundant product is methyl 2-methylepoxycarboxylate (2.2%) [6] which is probably formed by the following reaction.



As seen from Table 1, the T_{init} for the poly(methyl methacrylate) samples obtained with initiator **I** always, at any initiator concentration and cobalt content of the polymer, falls in the range 275–280°C, which is ~30°C higher than for the poly(methyl methacrylate) obtained with the benzoyl peroxide (**IV**) initiator. It should be noted that the cobalt content of the polymers are not proportional to the concentration of initiator **I** and increases with increasing reaction temperature. These features are explained by the inhibiting effect of β-diketonates on polymerization [13]. By contrast, T_{fin} is always proportional to the cobalt content of the polymer and is higher than that for the poly(methyl methacrylate) obtained with initiator **IV** by more than 20°C. When an equimolar mixture of initiators **I** and **IV** is used, T_{init} does not change, whereas T_{fin} increases considerably compared with that with the benzoyl peroxide initiator. The invariability of T_{init} is probably explained by the fact that there are certain saturating concentrations of inhibiting groups.

The saturating concentration of fullerenes C_{60} and C_{70} on methyl methacrylate polymerization is 4×10^{-3} mol kg^{-1} [7]. With ferrocene, the saturating concentration is even lower: 0.2×10^{-3} M [5]. In the AIBN-initiated methyl methacrylate polymerization in the presence of ferrocene, no correlation between T_{init} and ferrocene concentration was observed.

Table 1. Thermogravimetric characteristics of poly(methyl methacrylate) samples obtained at various initiator concentrations and reaction temperatures [conversion 10%, initiator cobalt(II) 3-allylpentane-2,4-dionate (**I**)]

Synthesis conditions				Characteristics		
$c_{in} \times 10^2$, M	T, °C	V_0, % h^{-1}	V_{av}, % h^{-1}	w_{Co}, wt %	T_{init}, °C	T_{fin}, °C
1.0[a]	70			–	250	392
1.0	60	7.0	4.2	0.015	280	395
1.0	70	14.0	4.8	0.025	280	405
1.0	85	32.4	11.3	0.080	275	415
0.5	70	24.9	10.2	0.033	287	412
0.1	70	11.4	7.7	0.024	279	410
1.0[b]	70	102.0	86.6	0.016	254	418

[a] Initiator benzoyl peroxide (**IV**). [b] Mixture of initiators **I** ($c_{\mathbf{I}}$ 1×10^{-2} M) and **IV** ($c_{\mathbf{IV}}$ 1×10^{-2} M).

The increased T_{init} and T_{fin} in the case of initiator **I** are explained by several reasons. It is commonly accepted that the value of the low-temperature characteristic T_{init} is associated with the degradation initiated by cleavage of unsaturated terminal groups formed by disproportionation. The enhanced stability of poly(methyl methacrylate) obtained in the presence of ferrocene is explained in terms of decreased number of unsaturated and formation of more stable ferrocene-containing terminal groups [5]. We previously showed that metal chelate groups in a polymerization system terminate propagation radicals and can prevent polymerization, when are present in high concentrations. Consequently, with complex **I** as initiator, the number of terminal groups will be low, and the terminal groups will be metal complexes; as a result, T_{init} will increase. Ruban and Zaikov in their review [4] have analyzed in detail the work of McNeil and Liggatt on the effect of cobalt(II) acetyacetonate on thermolysis of poly(methyl methacrylate). According to the statement of the latter referes, Co(*acac*)$_3$ does not form complexes with poly(methyl methacrylate), thermolysis involves the reaction Co(*acac*)$_3$ → Co(*acac*)$_2$ + *acac*·, and Co(*acac*)$_2$ forms a complex with poly(methyl methacrylate) carbonyl, which changes thermolysis mechanism and thermal stability. A series of reactions involving Co(*acac*)$_3$ and poly(methyl methacrylate) gives rise to anhydride rings that stabilize the polymer at high temperatures. In our case, the metal

Table 2. Thermogravimetric characteristics of poly(methyl methacrylates) at various conversions [initiator cobalt(II) 3-allylpentane-2,4-dionate (**I**), polymerization temperature 85°C, $c_{\mathbf{I}}$ 5×10^{-3} M]

Synthesis conditions			Characteristics					
S, %	V_0, % h^{-1}	V_{av}, % h^{-1}	w_{Co}, wt %	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	M_w/M_n	T_{init}, °C	T_{fin}, °C
13	62.0	18.2	0.058				271	408
35	62.0	17.0	0.038	1.45	5.00	3.45	270	415
87	62.0		0.021	2.40	10.00	4.17	274	415
30[a]	3.5	3.5	0.002	–	–	–	277	401

[a] Macroinitiator with a concentration of 2 wt %, obtained on methyl methacrylate polymerization, was used.

Table 3. Thermogravimetric characteristics of poly(methyl methacrylates) obtained in various solvents and at various initiator concentrations (temperature 70°C, conversion 10%)

Synthesis conditions				Characteristics			
solvent	$c_{in} \times 10^2$, M	V_0, % h^{-1}	V_{av}, % h^{-1}	w_{Co}, wt %	$M_{[\eta]} \times 10^{-5}$	T_{init}, °C	T_{fin}, °C
Toluene	1	11.7	10.3	0.067	6.25	277	410
Methyl ethyl ketone	2	30.0	22.6	0.085	1.80	272	415
DMF	25	13.2	6.6	0.190	4.34	267	440

chelate is not mechanically mixed with the polymers, as in [4], but is incorporated in the polymer. Nevertheless, here, too, anhydride rings can form at high temperature. As a result, T_{fin} increases proportionally to the content of metal chelate groups.

In the methyl methacrylate polymerization initiated by metal vinyl β-diketonates, metal complex fragments are incorporated in the macromolecule. The presence of active centers in the chain results in branching [12], and, therewith, branching is the stronger, the deeper polymerization. This enhances intermolecular interactions. If a polymer has a branched structure or cross-linked chains, the solubility of oxygen and its diffusion rate in the polymer are much lower, and such polymer is much more resistant to thermooxidative degradation [14]. Consequently, branching can be one more reason for stabilization. To verify this hypothesis, we studied the effect of conversion of the stability of the polymers (Table 2). As seen, with increasing conversion, the cobalt content of the polymer decrease and the molecular weight and polydispersity increase, on account of growth of new side chains. Therewith, T_{init} remains almost the same, whereas T_{fin} even increase, regardless of the fact that the content of metal chelates in the polymer decreases considerably. The highest degree of branching can be attained by using a macroinitiator, since in this case we deal with graft polymerization, and the cobalt concentration in the polymer is the lowest. However, T_{init} and T_{fin} are higher than with the benzoyl peroxide initiator.

The V_0 and V_{av} values in Table 2 much differ from each other, implying that polymerization slows down with increasing conversion and also that vinyl β-diketonates inhibit polymerization [13]. Consequently, branching and metal chelate groups are important factors that favor stability of poly(methyl methacrylate).

For increased concentration of metal chelate groups in the polymer we performed polymerization in solvents that dissolve vinyl β-diketonates better than the monomer (Table 3). Therewith, the V_0 and V_{av} in solvents only slightly differ from each other, and fairly fast polymerization occurs even at a high concentration of chelates in DMF. Consequently, solvents, being donor additives, enhances the initiative activity of β-diketonates, while the inhibiting effect of the latter remains the same [13], and the polymer contains adducts of β-diketonates with solvents rather than β-diketonates groups as such. Even though the cobalt

Table 4. Thermogravimetric characteristics of poly(methyl methacrylates) with various metal chelate (c_{in} 1×10^{-2} M, conversion 10%, temperature 70°C)

Synthesis conditions			Characteristics		
initiator	V_0, % h^{-1}	V_{av}, % h^{-1}	w_M, wt %	T_{init}, °C	T_{fin}, °C
I (Co)	14.0	4.8	0.025	280	405
II (Cu)	5.3	5.3	0.025	269	415
III (Ni)	–	–	0.038	270	405

contents of the polymer are high, T_{init} does not vary, and T_{fin} increases with increasing metal content.

We also studied the dependence of T_{init} and T_{fin} on the nature of the metal in vinyl β-diketonate (Table 4). As seen from Table 4, the TGA characteristics of copper(II) and nickel(II) chelates are close to those of cobalt(II) chelates. This corresponds to the results of Ruban and Zaikov [4] who showed that cobalt(II) and manganese(III) acetylacetonates similarly affect the T_{init} of poly-(methyl methacrylate) thermolysis [4].

EXPERIMENTAL

3-Allylpentane-2,4-dione and its metal complexes **I–III** were prepared as described in [15, 16]. The radical polymerization of methyl methacrylate was performed at varied concentrations of metal complexes, temperatures, and conversions. The process was performed in a block and in solvents (toluene, methyl ethyl ketone, and DMF). Polymer samples double reacrystallized from ethanol were studied under nonisothermal conditions. The T_{init} and T_{fin} values were calculated from the TG and DTA curves as described in [17].

Thermal analysis was performed on a Paulik–Paulik–Erdey instrument, temperature range 20–500°C, heating rate 10 deg min^{-1}. Analysis for metals was performed on a Saturn atomic absorption spectrophotometer.

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