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Copolymerization of Propylene and Methyl Vinyl Ketone with Metallocene Catalysts: Synthesis, Properties, and Thermal and Photooxidation of Modified Polypropylene

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Abstract—The copolymers of propylene and methyl vinyl ketone are synthesized at 60°C by copolymerization in the propylene bulk in the presence of the polymethylaluminoxane-activated metallocene catalysts, namely, the isospecific C_2-symmetric metallocene catalyst *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrCl_2$ and the syndiospecific C_s-symmetric metallocene catalyst $Ph_2CCpFluZrCl_2$, and characterized. It is shown that a noticeable insertion of methyl vinyl ketone into a polypropylene chain is possible during copolymerization initiated by the syndiospecific catalytic system, whereas in the case of the isospecific system, the insertion of methyl vinyl ketone is hindered. The thermal oxidation of the resulting polymers is studied. With the use of chemiluminescence, the accumulation of peroxy macroradicals under the action of daylight in samples based on isotactic and syndiotactic polypropylene is detected. It is found that even a low (0.2 mol %) content of methyl vinyl ketone endows polypropylene with the capability to undergo rapid and controlled degradation under natural conditions.

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Under natural conditions, the life span of the range of polymeric materials is several hundred years. Owing to the rapid development of polymer production, the environment is increasingly contaminated with polymer wastes. Therefore, the problems of endowing large-tonnage industrial polymers (polypropylene, polyethylene, and others) with photo-, thermal, and biodegradability for further utilization of their wastes has become urgent. One of the approaches to the creation of these materials is the synthesis of polymers containing oxygen-containing groups [1–4]. The presence of oxygen-containing groups in a polyolefin macromolecule increases the propensity of the polymer for photo- and thermal degradation under natural conditions [5, 6]. Since the mid-1980s [7–9], the synthesis and properties of alternating copolymers of olefins and CO have been an active area of research [10–12]. Under the action of light, the carbonyl group enters Norrish type I and type II reactions that lead to cleavage of the main polymer chain. Such degradation of a polymer into low-molecular-mass fragments requires a high (above 10 mol %) content of CO groups.

Another approach involves the creation of polymer composites based on polyolefins and components that can decompose under natural conditions. It likewise requires the use of a high content of degrading components. For example, a biodegradable polymer composite based on polyethylene contains 10–30% poly(methyl vinyl ketone) and polyhydroxybutyrate [13].

The application of a photoinitiator that possesses a higher initiation efficiency would make it possible to substantially reduce the initiator concentration required for polymer degradation. Previous investigations into photoinitiation in PP showed that the highest efficiency is manifested by photoinitiators that form a low-molecular-mass radical in the initiation event [14]. In this context, the introduction of a small amount of methyl vinyl ketone (MVK) into the PP chain via copolymerization is of particular interest. In this case, the Norrish type I reaction has the form

$$\mathrm{R{-}(CO){-}CH_3} + h\nu \rightarrow \mathrm{R}^\bullet$$
$$+ \mathrm{CH_3(CO)}^\bullet \rightarrow \mathrm{R}^\bullet + \mathrm{CO} + {}^\bullet\mathrm{CH_3},$$

where R is the PP macroradical, and yields low-molecular-mass radicals (acyl and methyl radicals), which, in subsequent reactions, give rise to macroradicals and chain oxidation of PP.

While the copolymers of ethylene and MVK are readily synthesized via radical polymerization [15], the copolymers of PP and MVK cannot be obtained the same way, owing to the low molecular masses of the resulting products [16]. Modern catalytic systems make it possible to copolymerize olefins and oxygen-containing compounds to produce copolymers with alternating internal and terminal carbonyl groups. The degrees of degradation of the polymeric products depend on the efficiency levels and amounts of the oxygen-containing groups introduced into the copolymers; therefore, the degrees of degradation of the materials may be finely tuned as early as during their synthesis. The presence of the carbonyl group in a polymer chain facilitates the interchain interaction. This circumstance strongly affects the mechanical and thermophysical properties of polymeric materials. Furthermore, the carbonyl group, being a potential reactive center, can be readily modified. This circumstance makes it possible to obtain new classes of functional compounds [17].

A number of reports have been devoted to the synthesis of copolymers based on olefins and polar comonomers containing carbonyl groups [18]. It was shown that the most promising catalysts, above all, for the production of ethylene-based copolymers, are chelate complexes of Pd and Ni. The metallocene complexes are usually rapidly deactivated during interaction with comonomers containing oxygen-containing fragments. The synthesis of the block copolymers of ethylene and methyl methacrylate over a $Me_2C(Cp)(Ind)ZrMe_2/B(C_6F_5)_3$ catalytic system was described in [19]. In the case of a sequential supply of ethylene and MMA, the polymerization of ethylene occurs over a cationic zirconium complex, and, when MMA is supplied, ethylene coordinates to the carbonyl groups of the comonomer and cationic metal-alkyl complexes are converted into cationic enolate complexes active in the polymerization of MMA. The fact that enolate complexes are responsible for the polymerization of carbonyl-containing monomers, including MVK, was mentioned in a number of other papers [20, 21].

Studies on the synthesis of copolymers of propylene and oxygen-containing comonomers are scarce. The two-stage synthesis of the block copolymers of propylene and MVK over heterogeneous isospecific Ziegler–Natta catalysts was reported in [22].

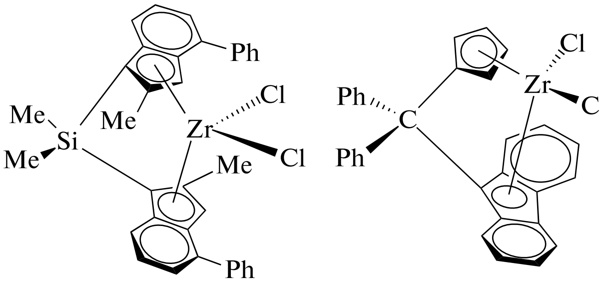
To modify PP and make it photodegradable, in this study, copolymers of propylene and MVK were synthesized in the medium of liquid propylene in the presence of polymethylaluminoxane-activated metallocene catalysts: the homogeneous isospecific C_2-symmetric ansa-metallocene catalyst *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrCl_2$ and the syndiospecific metallocene C_s-symmetric catalyst $Ph_2CCpFluZrCl_2$. Special attention was given to the effect of MVK additives on the properties of the modified PP: molecular-mass characteristics, macromolecular microstructure, thermophysical and mechanical characteristics, and features of the photo- and thermal oxidation of the polymer.

EXPERIMENTAL

In this study, polymerization-purity (99.9%) propylene was used without additional purification. Methyl vinyl ketone $CH_3COCH=CH_2$ (Aldrich) was distilled under argon over metallic sodium. Polymethylaluminoxane (MAO, Witco) was used in the form of a toluene solution (a concentration of 10 wt %).

The metallocene catalyst *rac*-dimethylsilylidenebis(2-methyl-4-phenylindenyl)zirconium dichloride (*rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrCl_2$, MC-1) was purchased from Boulder Scientific Co. The metallocene catalyst diphenylmethylidene(cyclopentadienyl)(fluorenyl)zirconium dichloride ($Ph_2CCpFluZrCl_2$, MC-2) was synthesized as described in [23].

MC-1 MC-2



(1)

All homo- and copolymerization experiments were performed with the use of preliminarily prepared 0.1–0.2% metallocene solutions in MAO. The propylene polymerization was performed on a unit with an autoclave-type reactor with a volume of 0.2 or 0.4 L in the mode of complete system filling with liquid propylene at 60°C. First, the unit was evacuated for 1 h at 60°C. The polymerization process was described in detail in [24]. During the synthesis of copolymers, various methods were used to introduce MVK into liquid propylene: (i) 10–20 min after the beginning of the experiment and (ii) in portions in the course of the experiment. After completion of the polymerization, the polymer powder was retrieved from the reactor, washed from the residual components of the catalytic system with a mixture of ethanol and hydrochloric acid (a 5% solution), and dried under vacuum at 60°C.

The microstructures of the polymer samples were determined via IR spectroscopy on a Vertex 70 FTIR spectrometer (Bruker). The stereoregularity of the samples based on isotactic PP was estimated from the ratio of optical densities of absorption bands at 998 and 973 cm^{-1}, D_{998}/D_{973}, which characterizes the fraction of isotactic sequences of propylene units with lengths more than 11–13 monomer units in the polymer chain [25]. For the samples based on syndiotactic

Table 1. Effect of polymerization conditions on the activity of the MC-1–MAO catalytic system and characteristics of the polymers ($T = 60°C$, liquid propylene)

Sample	Zr × 10^{-7}, mol	Al/Zr	MVK content in the monomer mixture, mol %	Experiment time, min	Yield, g	Activity, kg polymer/(mmol Zr h)	D_{998}/D_{973}	$M_w \times 10^3$	M_w/M_n
IPP	1.0	35000	0	30	22	440	0.87	520	2.0
IPP–MVK-1*	2.1	22700	0.2	60	9	43	0.89	550	1.9
IPP–MVK-2**	2.2	20400	1.8	50	10	54	0.87	480	1.9
IPP–MVK-3***	2.0	22100	2.1	30	5	50	0.90	680	2.1

*MVK was introduced at the 17th min of the experiment.

**MVK was introduced portionwise from the 20th minute of the experiment.

***MVK was introduced at the beginning of the experiment (at the 10th min).

PP (SPP), stereoregularity was estimated from the ratio of intensities of bands at 1155 and 870 cm^{-1}, in accordance with [25].

The contents of carbonyl groups in the copolymers were estimated from the IR absorption band at 1705 cm^{-1} with the use of the ketone extinction coefficient in PP (~220 L/(mol cm)) [26].

The molecular-mass characteristics of the polymers were determined via GPC on a Waters GPCV-2000 chromatographer equipped with a PL-gel column and a refractometer. Measurements were performed at 135°C in 1,2,4-trichlorobenzene; the rate of elution was 1 mL/min. The average molecular mass was calculated from the universal calibration curve constructed relative to PS standards.

The thermophysical characteristics of the polymers (temperature and heats of melting and crystallization) were determined on a PerkinElmer DSK-7 calorimeter at a heating–cooling rate of 10 K/min. The enthalpy of melting of PP with a degree of crystallinity of 100% was taken to be 167 J/g [27].

The samples for mechanical tests were prepared by pressing of the polymers at a temperature of 190°C, a pressure of 10 MPa, and a melt cooling rate of 16 K/min. The tensile tests were performed at 20°C on an Instron 1122 testing machine with the use of samples with a cross section of 0.5 mm × 5.0 mm and a gage length of 35 mm.

The thermal oxidation of the polymer samples was studied in the kinetic mode at temperatures of 120 and 130°C and an oxygen pressure of 300 mmHg [28]. The kinetics of oxygen absorption was investigated on a highly sensitive manometric unit. Solid KOH was used as an absorber for volatile products.

To study chemiluminescence, thin polymer films were irradiated in air at 23°C with the light of a DBU-30 day lamp (with a wavelength above 300 nm). The irradiated samples were placed in the chamber of an SNK-7 unit [29], where the intensity of chemiluminescence was measured. (Measurements were started 1 min after the onset of irradiation.)

RESULTS AND DISCUSSION

Copolymerization of Propylene and MVK

Table 1 shows the data on the homopolymerization of propylene and its copolymerization with MVK performed with the use of isospecific metallocene MC-1 activated with MAO. It is seen that the introduction of MVK into the reaction medium leads to a drastic drop in the rate of polymer formation from 440 to 65 kg polymer/(mmol Zr/h). Note that the stereoregularity of PP remains almost the same.

Figure 1 presents the kinetic curves for the homo- and copolymerization of propylene and MVK with the use of the MC-1–MAO system.

In the case of propylene homopolymerization, the obtained kinetic curve is typical for this system and corresponds to propylene polymerization in the monomer bulk [30].

The introduction of MVK substantially reduces the catalyst activity. The portionwise introduction of MVK has the lowest effect on change in the activity of the catalytic system with time (Fig. 1, curve *3*).

For the samples based on isotactic PP, the absorption of CO groups in the IR spectra is low; the maximum observed content of CO is estimated as 0.02 mol % in the IPP–MVK-3 sample.

Table 2 and Fig. 2 present the data on the homopolymerization of propylene and its copolymerization with MVK in the presence of syndiospecific metallocene MC-2 activated with MAO. The results on the homopolymerization of SPP (SPP-1 and SPP-2) provide evidence for the good reproducibility of the experiments.

In this case, MVK was introduced at the fifteenth minute of the experiment. It is obvious that the intro-

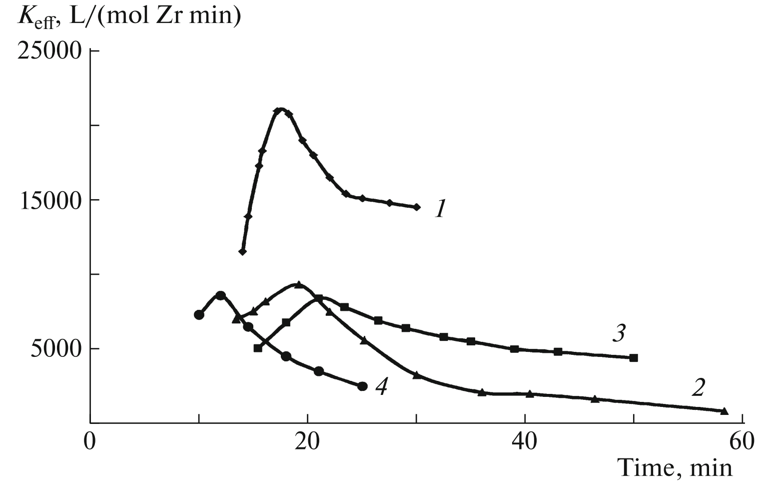


Fig. 1. Kinetic curves for the homopolymerization and copolymerization of propylene with the use of MC-1–MAO: (*1*) PP polymerization (Table 1); (*2*) MVK was introduced at the 17th minute of the experiment; (*3*) MVK was introduced portionwise from the 20th minute of the experiment; and (*4*) MVK was introduced at the beginning of the experiment.

duction of MVK into the reaction medium also substantially decreases the rate of polymer formation.

Note that the syndiospecific system affords higher MVK contents (up to 0.2 mol %) in polymers than those afforded in the case of the isospecific system.

It may be assumed that the sterically hindered active center of the isospecific C_2-symmetric catalyst bearing substituted indenyl ligands is less favorable for the insertion of MVK than the more accessible active center of the syndiospecific C_s-symmetric catalyst.

The IR spectral analysis of the microstructures of the polymers obtained with the syndiospecific catalyst testifies that the stereoregularity of the polymer chain is substantially lower. This finding may be associated with a high content of CO groups in the polymer chain, at which the disordering effect of the comonomer becomes more pronounced.

Tables 1 and 2 present the molecular-mass characteristics of the resulting polymers. It is obvious that the molecular masses of the polymers slightly change with an increase in the content of MVK units. It is interesting that the copolymerization of propylene with ethylene and higher olefins over these catalysts usually affords lower molecular mass polymers [31–33], a result that is usually explained by the β-hydride transfer to the monomer [34].

Thermophysical Characteristics of the Polymers

Table 3 shows the temperatures of melting and crystallization and the heats of melting and crystallization for the polymers obtained with the isospecific metallocene catalytic system MC-1–MAO.

The values of melting temperatures measured during the first and second heating runs differ insignificantly and decrease with an increase in the MVK content. Reductions in the melting temperature by 3 and 5°C during the first and second heating runs indicate that the sizes of PP crystallites obtained in the presence of MVK are smaller. The same is evidenced by the finding that the enthalpy of melting decreases by 10 J/g.

Interestingly, the introduction of a small amount of MVK into the chain of isotactic PP leads to an increase in the crystallization temperature of almost 9°C; this result is likely connected with the appearance of new crystallization centers that is due to a decrease

Table 2. Effect of polymerization conditions on the activity of the MC-2–MAO catalytic system and characteristics of the polymers ($T = 60$°C, liquid propylene)

Sample	$\text{Zr} \times 10^{-7}$, mol	Al/Zr	MVK content in the monomer mixture, mol %	Experiment time, min	Yield, g	Activity, kg polymer/(mmol Zr h)	[CO] in copolymer, mol %	D_{870}/D_{1155}	$M_w \times 10^3$	M_w/M_n
SPP-1	8.37	7000	0	55	15	20	0	0.69	315	2.3
SPP-2	7.84	7000	0	40	16	30	0	0.72	320	2.3
SPP–MVK-1	9.42	6400	0.4	70	1	0.9	~0.2	0.61	301	3.3
SPP–MVK-2	10.21	6500	1.2	67	2	1.8	0.2	0.55	307	3.4

in the local mobility of chains during the formation of hydrogen bonds between the ketone and PP. A similar effect was observed for the copolymers of propylene and vinylcyclohexane, where the local restriction in mobility is caused by the large volume of the comonomer [35].

Table 4 presents the data on the temperatures of melting and crystallization and the heats of melting and crystallization of SPP and SPP copolymers with MVK obtained with the use of the MC-2–MAO catalytic system. It is apparent that the melting temperature and enthalpy of melting decrease with the introduction of MVK units. This outcome indicates a decrease in the crystallite sizes, as in the case of the IPP–MVK samples.

After the introduction of MVK units, the crystallization temperatures decrease. This situation is unlike that observed in the case of the isospecific system (Table 3). It may be assumed that the comonomer with polar groups has a double effect on the crystallization of PP. On the one hand, it acts as a nucleating agent that forms hydrogen bonds and reduces the mobility of PP chains. As a result, the T_{cr} of the polymer increases. On the other hand, the comonomer worsens the tacticity of PP via disruption of regular sequences of propylene units. As a result, the T_{cr} of the polymer decreases. At a low content of MVK, when its amount is insufficient to decrease tacticity (as in the case of the IPP–MVK samples, Table 1), only its nucleating effect manifests itself. At a higher content of MVK, which can be achieved with the syndiospecific system, the disordering effect assumes importance: In the SPP–MVK samples, the tacticity is much lower (Table 2) and T_{cr} drops. A marked decrease in T_{cr} due to the disordering effect of comonomers introduced into the PP chain was observed for the propylene copolymers with linear olefins [31–33].

Mechanical Characteristics of the Polymers

Table 5 lists the stress–strain characteristics of the polymers synthesized with the use of the isospecific and syndiospecific catalytic systems.

As is seen from Table 5, the introduction of a small amount of MVK units into IPP and SPP causes a noticeable modification of the properties of polypropylene.

For the IPP-based polymers, the elastic moduli remain almost the same. However, the rupture strain decreases substantially. This fact indicates that brittleness grows after the introduction of MVK units into the polymer chain.

Another picture is observed for the polymers based on SPP. The elastic modulus slightly decreases, while the rupture stress increases and the elongation at break grows considerably. The material becomes more plastic. It may be assumed that, after the introduction of ketones into SPP, the interchain hydrogen bond becomes weaker than that in IPP.

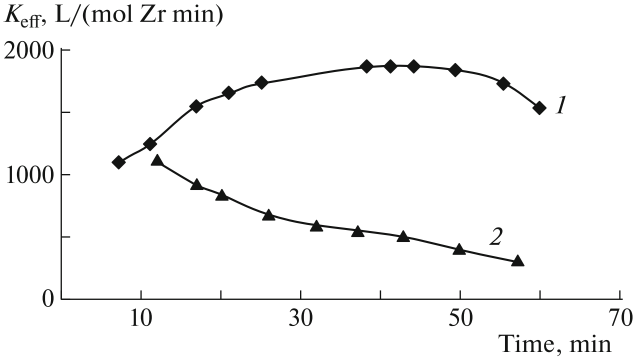


Fig. 2. Kinetic curves for polymerization with the use of the MC-2–MAO system: (*1*) propylene homopolymerization (SPP-1 synthesis, Table 2) and (*2*) MVK was introduced at the 15th minute of the experiment (SPP–MVK-1 synthesis).

Oxidation of the Polymers

The degradation of PP primarily occurs by chain oxidation of PP peroxy macroradicals and is accompanied by degenerated branching on hydroperoxides [28]. The kinetics of oxidation of IPP, SPP, and propylene copolymers with MVK at temperatures below their melting temperatures are presented in Figs. 3 and 4. The MVK-containing polymers (based on both IPP and SPP) oxidize much faster than the homopolymers.

For the IPP copolymers with a low content of MVK, the induction period undergoes practically no change and the oxidation rate increases substantially. As the content of MVK is increased, the induction period shortens by a factor of 2. For the SPP copolymer containing 0.2 mol % MVK, the induction period shortens by a factor of 4. Hence, the introduction of MVK into the PP chain even at small concentrations strongly changes the kinetics of oxygen absorption: The induction period substantially decreases, and the maximum oxidation rate increases.

Table 3. Thermophysical characteristics of the polymers obtained with the use of MC-1–MAO

Sample	T_{m1}, °C	ΔH_{m1}, J/g	K, % (DSC)	T_{m2}, °C	ΔH_{m2}, J/g	T_{cr}, °C
IPP	162.0	90.6	55	163.0	89.3	114.0
IPP–MVK-1	160.9	89.6	54	159.9	87.4	122.3
IPP–MVK-2	160.9	80.0	48	158.6	89.0	114.0
IPP–MVK-3	159.0	80.0	48	158.0	79.2	123.3

Table 4. Thermophysical characteristics of the polymers obtained with the use of MC-2–MAO

Sample	T_{m1}, °C	ΔH_{m1}, J/g	K, % (DSC)	T_{m2}, °C	ΔH_{m2}, J/g	T_{cr}, °C
SPP-1	131.4/138.3	48.8	28	138.8	47.2	107
SPP–MVK-1	137	45.0	27	135.0	38.0	97
SPP–MVK-2	128.5/135.8	45.9	27	130.9	40.1	68.4

Table 5. Mechanical properties of the resulting polymers

Sample	E, MPa	σ_h, MPa	ε_h, %	σ_b, MPa	ε_b, %
IPP	1103	36.8	7.0	30.6	289
IPP–MVK-1	1110	35.7	6.1	27.0	62
IPP–MVK-2	1085	36.9	7.4	33.1	11
SPP-2	490	18.0	10.2	13.5	180
SPP–MVK-2	407	16.7	11.6	23.4	406

It is known that, at the initial stage of the uninhibited oxidation of polyolefins, the kinetics of oxygen absorption is described by a parabolic law [28]:

$$N_{O_2} = b^2(t - \tau)^2,$$

where N_{O_2} is the amount of absorbed oxygen; t is the time; and τ and b are the induction period and the kinetic parameter of oxidation, respectively.

These values are as follows:

$$\tau = k/\alpha\sigma k_2 k_4[\mathrm{RH}]^2, \quad (1)$$

$$b = (\alpha\sigma k_2^2 k_4[\mathrm{RH}]^3/8k_6)^{1/2}, \quad (2)$$

where k is the rate constant of linear termination; k_2 and k_6 are the rate constants of oxidation chain propagation and termination, respectively; k_4 is the rate constant of hydroperoxide decomposition; α is the yield of hydroperoxide per mole of absorbed oxygen; σ is the probability of degenerated branching of kinetic oxidation chains; and [RH] is the concentration of the reactive bonds.

As can be seen from Eq. (1), a decrease in the induction period can result from the simultaneous changes of several kinetic parameters. In our opinion, it is most probable that the reduction of the induction period is due to a decline in the rate of radical termination, which is expected for the PP copolymers with ketone because the mobility of chains is reduced owing to the formation of hydrogen bonds. Moreover, the induction period may become shorter owing to an increase in the escape of radicals from the cage. This phenomenon is expected for the copolymers because the local mobility of chain segments due to disruption of the regularity, as manifested by a reduction in T_{cr} of SPP. An increase in the oxidation rate after completion of the induction period, in accordance with Eq. (2), likewise can result from simultaneous changes in several kinetic parameters both due to an increase in the escape of radicals from the cage and due to a reduction in the rate of quadratic termination of radicals.

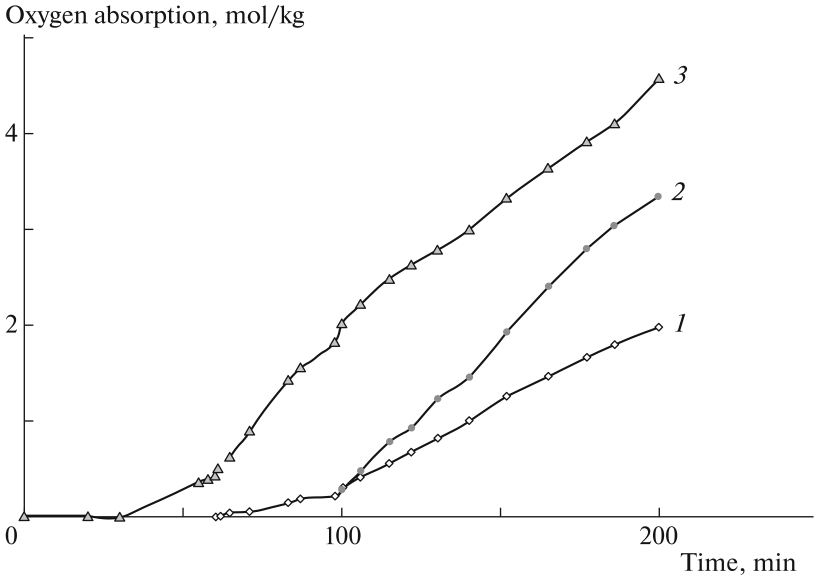


Fig. 3. Thermal-oxidation curves for the samples based on IPP at 130°C: (*1*) IPP, (*2*) IPP–MVK-1, and (*3*) IPP–MVK-2.

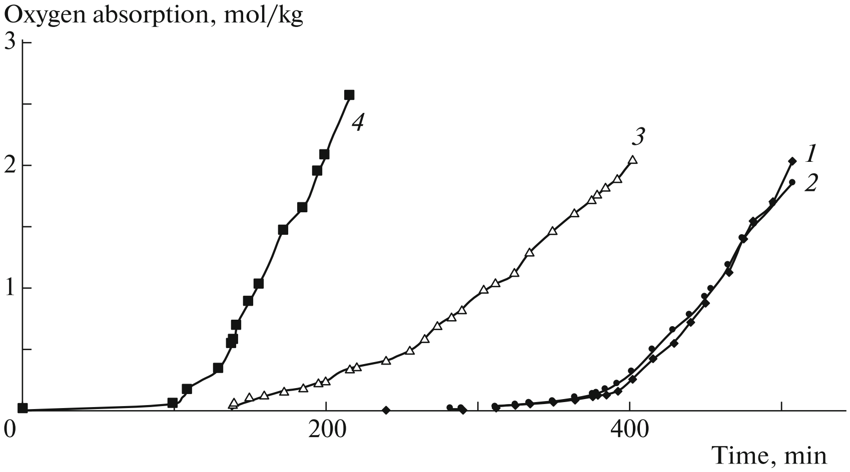


Fig. 4. Thermal-oxidation curves for the samples based on SPP at 120°C: (*1*) SPP-1, (*2*) SPP-2, (*3*) SPP–MVK-1, and (*4*) SPP–MVK-2.

Chemiluminescence of the Polymers

The chemiluminescence of PP arises during the reaction of termination of peroxy PP macroradicals that are formed under the action of light and oxygen [36]. It is known that, at a low concentration of the radicals, this reaction is of the first order with respect to the radical concentration (the linear termination of oxidation chains) [28]; as a consequence, the intensity of PP chemiluminescence, *I*, at room temperature is proportional to the rate of termination of peroxy macroradicals and their concentration [36]:

$$I = \phi k[\mathrm{RO_2}], \tag{3}$$

where ϕ is the quantum yield of chemiluminescence (the number of light quanta per act of radical termination), k is the rate constant of radical termination, and $[\mathrm{RO_2}]$ is the concentration of peroxy radicals.

According to Eq. (3), the intensity of chemiluminescence is directly proportional to the concentration of peroxy macroradicals, $[\mathrm{RO_2}]$. Therefore, the measurement of chemiluminescence intensity makes it possible to ascertain a change in the concentration of PP radicals.

The method of chemiluminescence was used to study the accumulation of peroxy radicals in the samples based on IPP and SPP during irradiation with a daylight lamp at 23°C. The dependence of chemiluminescence intensity of the resulting polymers on the irradiation time is depicted in Fig. 5. Prior to irradiation, no chemiluminescence was detected in the samples. This finding shows that, at room temperature, no dark oxidation of PP and no accumulation of peroxy radicals occur.

The irradiation of the SPP films with daylight does not afford chemiluminescence (Fig. 5, curve *1*). The irradiation of the IPP films with daylight affords a slight increase in the luminescence intensity at the beginning of irradiation and disappears after further irradiation (Fig. 5, curve *2*). Such a reduction in the luminescence intensity indicates burning of impurities under the action of light. This process is most likely not connected with the oxidation of IPP.

Under the action of daylight, the polymers with MVK manifest chemiluminescence, whose intensity grows in the course of irradiation (Fig. 5, curves *3*, *4*). The effect of luminescence intensification has two causes. First, the time of peroxy radical termination in PP amounts to several minutes [28], therefore, establishment of the stationary concentration of radicals takes a long time. Second, the decomposition of keto groups under the action of light does not lead to a decrease in their concentration and is compensated by their formation during the chain oxidation of PP, when tens of keto groups are formed in the acts of chain propagation per keto group disappearing from the photoinitiation act.

As can be seen from Fig. 5, the oxidation of SPP with MVK (curve *4*) proceeds at much (5–6 times) higher concentrations of the peroxy radicals than the oxidation of IPP with MVK (curve *3*). This circumstance is due to a higher content of keto groups in the sample based on syndiotactic PP than that in the samples based on isotactic PP.

Hence, the resulting copolymers of propylene and MVK, especially those based on SPP, are sensitive to daylight at room temperature. This circumstance testifies their high propensity toward photodegradation under natural conditions.

In this study, new copolymers of propylene and MVK were synthesized and characterized. These copolymers carry side keto groups and possess the ability to decompose under daylight at a very low content of these groups (0.02–0.2 mol %) while retaining the main performance characteristics of PP. Note that

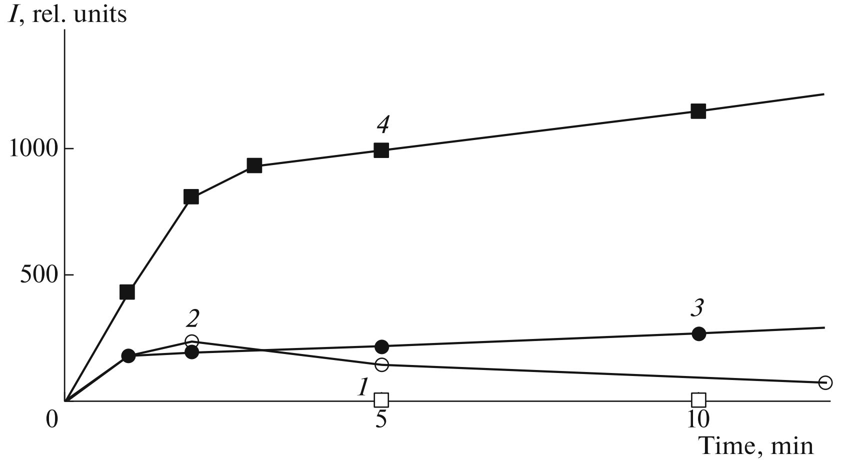


Fig. 5. Evolution in intensity of chemiluminescence of polymer and copolymer films with the time of irradiation with a daylight lamp at room temperature in air for samples of (*1*) SPP-2, (*2*) IPP, (*3*) IPP–MVK-2, and (*4*) SPP–MVK-1.

the achieved high rates of photooxidation of the studied polymers offer prospects for the controlled photodegradation of PP. It is important that a decrease in the rate of PP photooxidation can be achieved either by a decrease in the MVK content in the monomer mixture or by the addition of small amounts of the resulting copolymer to PP.

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