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MACROMOLECULAR CHEMISTRY
AND POLYMERIC MATERIALS

Structural-Group Composition of Low-Molecular-Weight Products of Thermal Oxidative Degradation of Atactic Polypropylene

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Abstract—The composition and structure of low-molecular-weight products of thermal oxidative degradation of atactic polypropylene were studied.

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Atactic polypropylene (APP) is a by-product from production of isotactic polypropylene [1, 2]. It is a rubber-like material with high fluidity, melting point of approximately 80°C, and density of 850 kg m^{-3}; it is well soluble in organic solvents.

Atactic polypropylene has a number of properties opening prospects for its useful utilization. Products of APP chemical modification have been in demand in the past decade. They are used as components of new composite materials for industry, housing, and road building, as components of adhesive compounds, and as modifying additives to liquid hydrocarbon fuels and various technical oils [3, 4].

One of methods for chemical modification of APP is its thermal oxidative degradation (TOD) [5]. Studies of the polypropylene oxidation and of products formed in the process are of interest for estimating the working life of polymer items and the environmental impact of polymer wastes [6–9].

The low-molecular products of APP TOD are wastes from production of oxidized APP, which is produced on a semicommercial installation with an annual capacity of 400 t. The yield of low-molecular-weight compounds depends on the reaction temperature and varies within 0.7–5.0 wt % [10].

Previously [10, 11] we studied the general characteristics of the composition and structure of low-molecular-weight products of APP TOD and the structure of the polymeric product itself.

In this study we examined the structural-group composition and structure of low-molecular-weight products of APP TOD with the aim to determine the most appropriate fields of their use.

EXPERIMENTAL

Thermal oxidative degradation of APP (Tomskneftekhim Limited Liability Company) was performed by oxidation of APP melt with atmospheric oxygen at 200°C for 2 h on a semicommercial installation using continuous synthesis scheme. Liquid low-molecular-weight products of APP oxidation are pale yellow with a density at 20°C of 0.80 g cm^{-3}, refractive index at 20°C of 1.4485, and kinematic viscosity at 20°C of 13.9 mm^2 s^{-1}; they are distilled at atmospheric pressure in the temperature range 80–305°C.

Fractionation of the condensed mixture of low-molecular-weight organic compounds was performed on a column packed with silica gel. Elution was performed in succession by hexane, chloroform, and chloroform–ethanol mixture (1 : 1). The solvents were distilled off under vacuum. The composition of the fractions obtained was studied by gas chromatography–mass spectrometry (GC–MS) and IR spectroscopy.

The IR spectra were recorded on a Spectrum-100 device (Perkin–Elmer) in NaCl cells with a layer thickness of 0.1 mm; carbon tetrachloride was used as solvent.

The GC–MS analysis was performed with a Clarus 500MS device (Perkin–Elmer) using a capillary

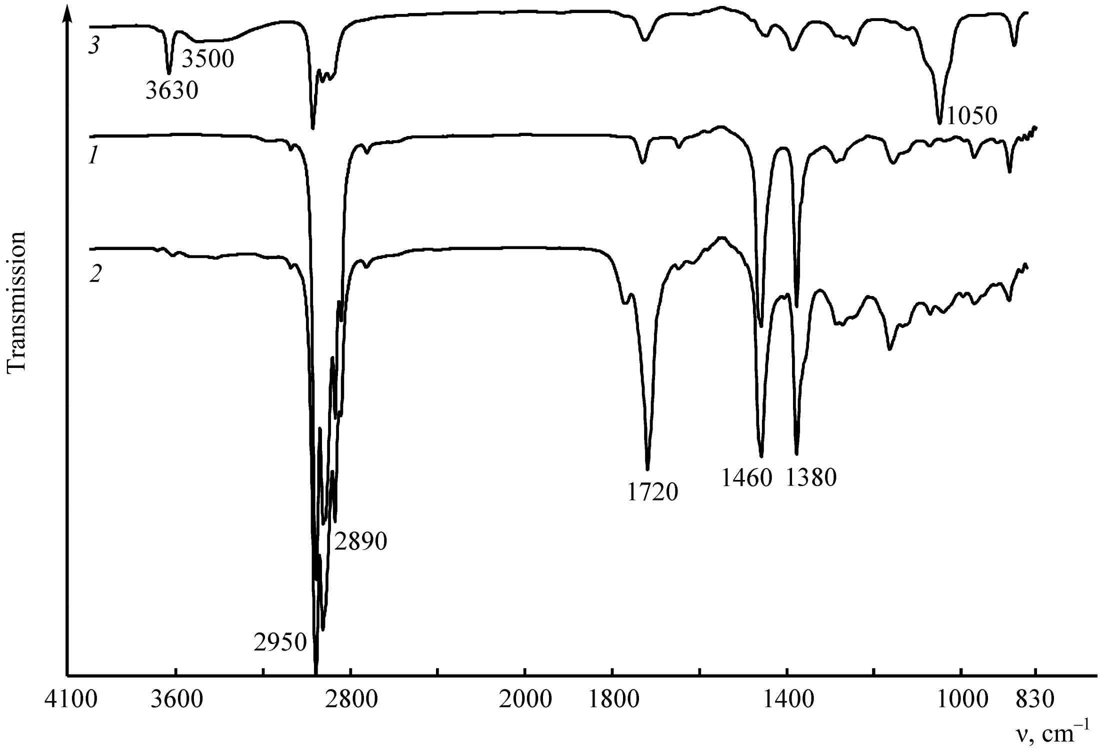


Fig. 1. IR spectra of fractions of low-molecular-weight APP oxidation products. (ν) Wavenumber. Fraction: (*1*) hexane, (*2*) chloroform, and (*3*) chloroform–alcohol.

column coated with SE-54 (L = 30 m, d = 0.25 mm). The column temperature schedule was as follows: 80°C, 3 min; heating at a rate of 10 deg min^{-1} to 280°C. Vaporizer temperature 250°C, flow rate of the carrier gas (He) 0.5 cm^3 min^{-1}. Ionization by electron impact, ionizing electron energy 70 eV.

The IR spectrum of the hexane fraction of the low-molecular-weight oxidation products (Fig. 1) shows that it mainly consists of saturated hydrocarbons. The presence of a large amount of aliphatic structures is confirmed by strong absorption bands of C–H stretching and bending vibrations in $>CH_2$ and $-CH_3$ groups at 3000–2800, 1460, and 1380 cm^{-1} [12]. The IR spectrum of the chloroform fraction also contains strong bands of C–H stretching and bending vibrations in $>CH_2$ and $-CH_3$ groups at 3000–2800, 1460, and 1380 cm^{-1}, and also a medium-intensity band at 1720 cm^{-1}, characteristic of stretching vibrations of the carbonyl group –C=O in ketones.

In the IR spectrum of the chloroform–alcohol fraction containing the most polar compounds, in the range 3500–3200 cm^{-1} there is a broad absorption band characteristic of stretching vibrations of the bound hydroxy group. In addition, in the IR spectrum of the concentrated solution of the chloroform–alcohol fraction (Fig. 2) there are additional absorption bands with maxima at 1640, 1324, and 1090 cm^{-1}. The band at 1324 cm^{-1} is assigned to interaction between O–H in-plane bending vibrations and C–O stretching vibrations in hydrogen-bonded dimers [13]. A strong absorption band with a maximum at 1090 cm^{-1} is characteristic of stretching vibrations of the C–O bond of the hydroxy group. Strong bands with maxima at 1050 and 3630 cm^{-1} are characteristic, respectively, of stretching vibrations of the C–O bond and free hydroxy group in alcohols C–O–H. Thus, the IR spectrum of the chloroform–alcohol fraction is indicative of the presence of ketones, alcohols, and a small amount of carboxylic acids.

The fractions obtained were subjected to a GC–MS analysis. The chromatogram of the hexane fraction, plotted on the total ion current scale, is shown in Fig. 3. The group identification based on characteristic ions [14] allowed a conclusion that the hexane fraction mainly consists of branched saturated (C_nH_{2n+2}) and unsaturated (C_nH_{2n}) hydrocarbons. In the chromatogram there are recurrent groups of peaks belonging to alkanes and alkenes: C_{12} (with the strongest peak at

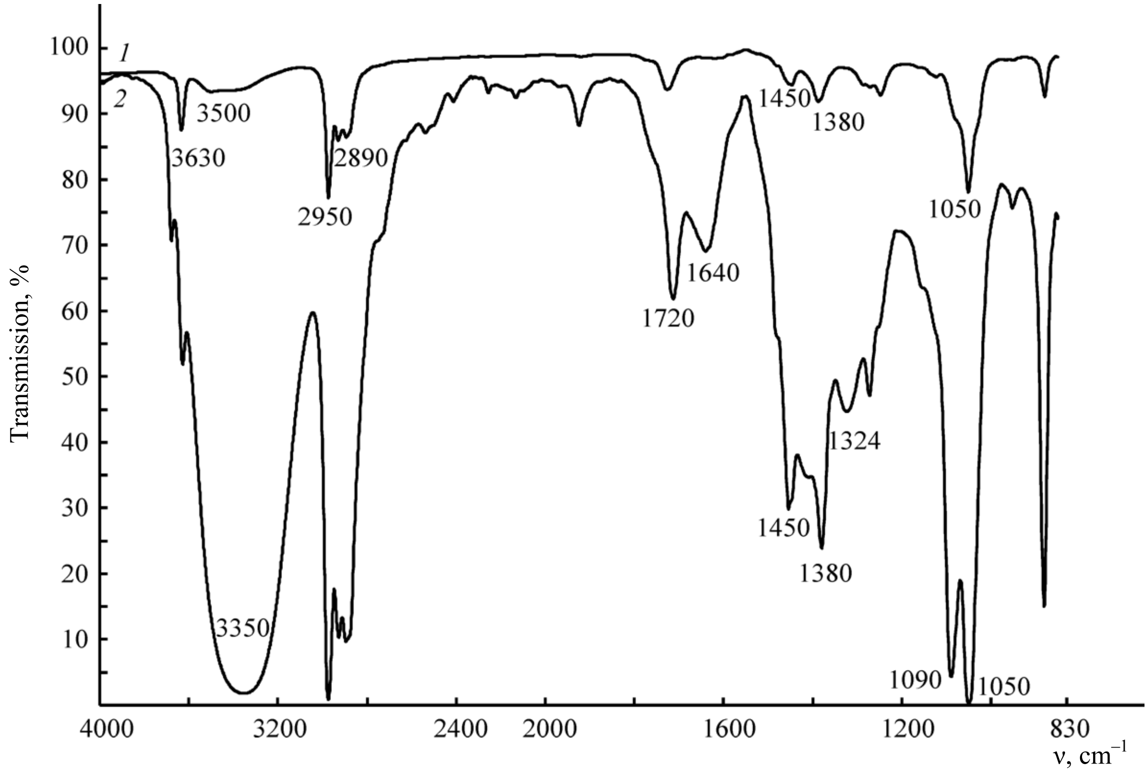


Fig. 2. IR spectra of the chloroform–alcohol fraction. (ν) Wavenumber. Sample: (*1*) dilute and (*2*) concentrated.

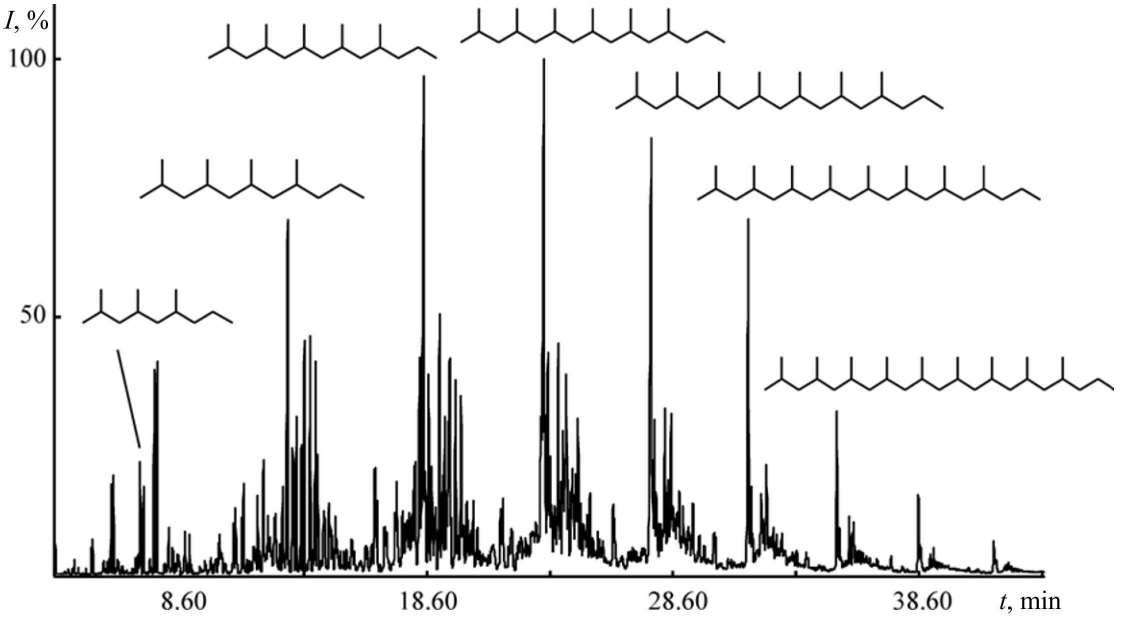
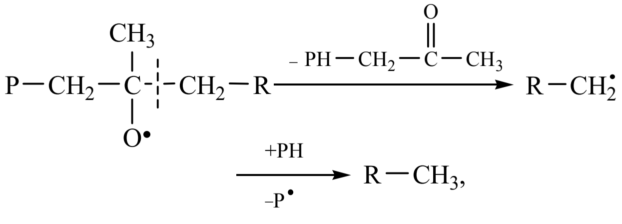


Fig. 3. Chromatogram of the hexane fraction of low-molecular-weight APP oxidation products. (*I*) Peak intensity and (*t*) retention time; the same for Figs. 5 and 7.

6.95 min), C_{15} (12.95 min), C_{18} (18.48 min), C_{21} (23.36 min), C_{24} (27.72 min), C_{27} (31.67 min), C_{30} (35.27 min), and C_{33} (38.57 min). This periodicity corresponds to an increment of $–C_3H_6$ in going from each group to the subsequent group.

The homology observed in the series of low-molecular-weight alkanes is an experimental confirmation of random cleavage of the APP chain (closer to the macromolecule terminus) in the course of TOD. The oxidation mainly occurs at the tertiary carbon atom with intermediate formation of hydroperoxides. Polymethyl-substituted alkanes are formed by α-cleavage of alkoxyl radicals:

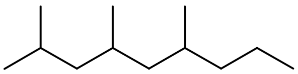


$$\mathrm{P-CH_2-\overset{CH_3}{\underset{O^\bullet}{C}}-CH_2-R} \xrightarrow{-\mathrm{PH-CH_2-\overset{O}{\overset{\|}{C}}-CH_3}} \mathrm{R-\dot{C}H_2} \xrightarrow[-\mathrm{P}^\bullet]{+\mathrm{PH}} \mathrm{R-CH_3},$$

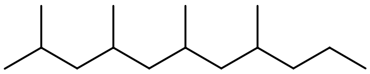
where P and R are the polymeric and alkyl radicals, respectively.

The strongest peaks with the above-indicated retention times correspond to branched saturated hydrocarbons with the empirical formulas $C_{12}H_{26}$, $C_{15}H_{32}$, $C_{18}H_{38}$, $C_{21}H_{44}$, $C_{24}H_{50}$, $C_{27}H_{56}$, $C_{30}H_{62}$, and $C_{33}H_{68}$, respectively. Figure 4 shows the mass spectra of isoparaffins $C_{15}H_{32}$–$C_{27}H_{56}$. As can be clearly seen, the mass spectra exhibit the same set of fragment ions with similar intensity distributions (*m*/*z* 43, 57, 71, 85, 99, 113, 127, 141, 155, 169); hence, these molecules have similar fragmentation patterns. Based on the fragmentation patterns of these compounds, their most probable structural formulas were suggested:

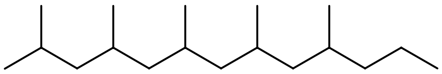
$C_{12}H_{26}$



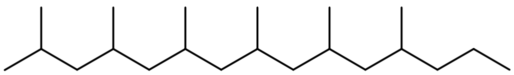
$C_{15}H_{32}$



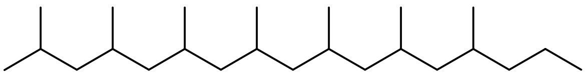
$C_{18}H_{38}$



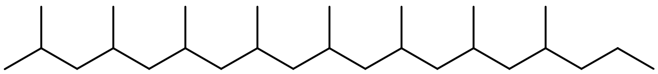
$C_{21}H_{44}$



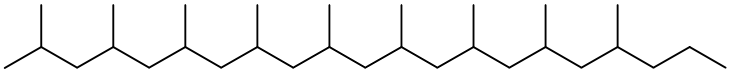
$C_{24}H_{50}$



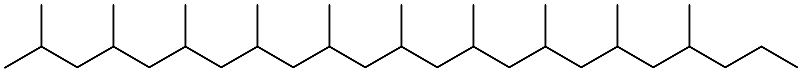
$C_{27}H_{56}$



$C_{30}H_{62}$

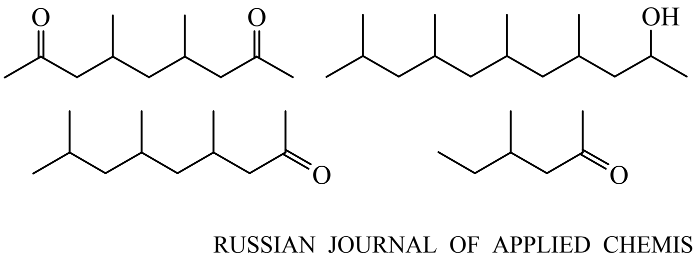


$C_{33}H_{68}$



As follows from these structural formulas, the terminal fragments of the most abundant hydrocarbons are the same in the entire interval of molecular weights.

The polar fractions differ in the composition from the hexane fraction by the presence of polar oxygen-containing compounds. Figure 5 shows the chromatogram of the chloroform fraction of low-molecular-weight products of APP oxidation. This chromatogram is also characterized by a sequence of recurrent peaks with an interval corresponding to the $-C_3H_6-$ fragment. Figure 6 shows the mass spectra corresponding to the strongest chromatographic peaks in the recurrent groups. Their analysis allows the corresponding compounds to be identified as branched ketones. In their mass spectra, there are also similar sets of fragmentation peaks. The structure of alkyl chains of ketones depends on the presence in APP macromolecule of units with anomalous tail-to-tail linkage and of branching sites in the backbone [11]. Below are the structures of oxygen-containing compounds identified in the chloroform fraction:



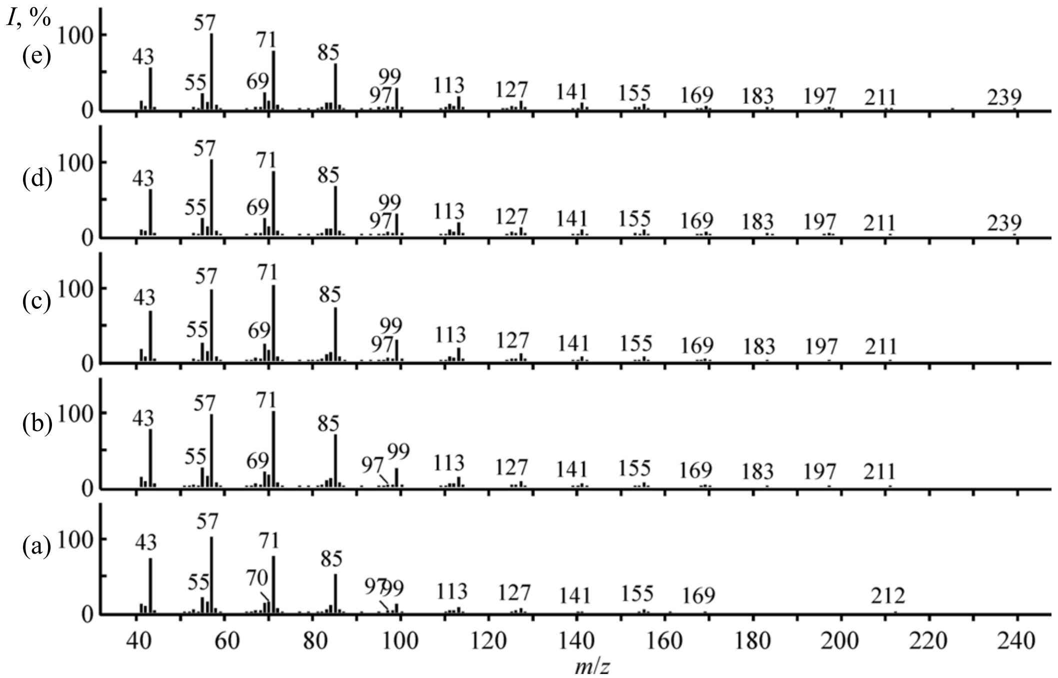


Fig. 4. Mass spectra corresponding to the strongest chromatographic peaks of isoparaffins shown in Fig. 3. (*I*) Intensity; the same for Fig. 6. (a) 2,4,6,8-Tetramethylundecane $C_{15}H_{32}$, $M^{+\cdot}$ = 212 Da (12.95 min); (b) 2,4,6,8,10-pentamethyltridecane $C_{18}H_{38}$, $M^{+\cdot}$ = 254 Da (18.47 min); (c) 2,4,6,8,10,12-hexamethylpentadecane $C_{21}H_{44}$, $M^{+\cdot}$ = 296 Da (23.36 min); (d) 2,4,6,8,10,12,14-heptamethylheptadecane $C_{24}H_{50}$, $M^{+\cdot}$ = 338 Da (27.72 min); and (e) 2,4,6,8,10,12,14,16-octamethylnonadecane $C_{27}H_{56}$, $M^{+\cdot}$ = 380 Da (31.67 min).

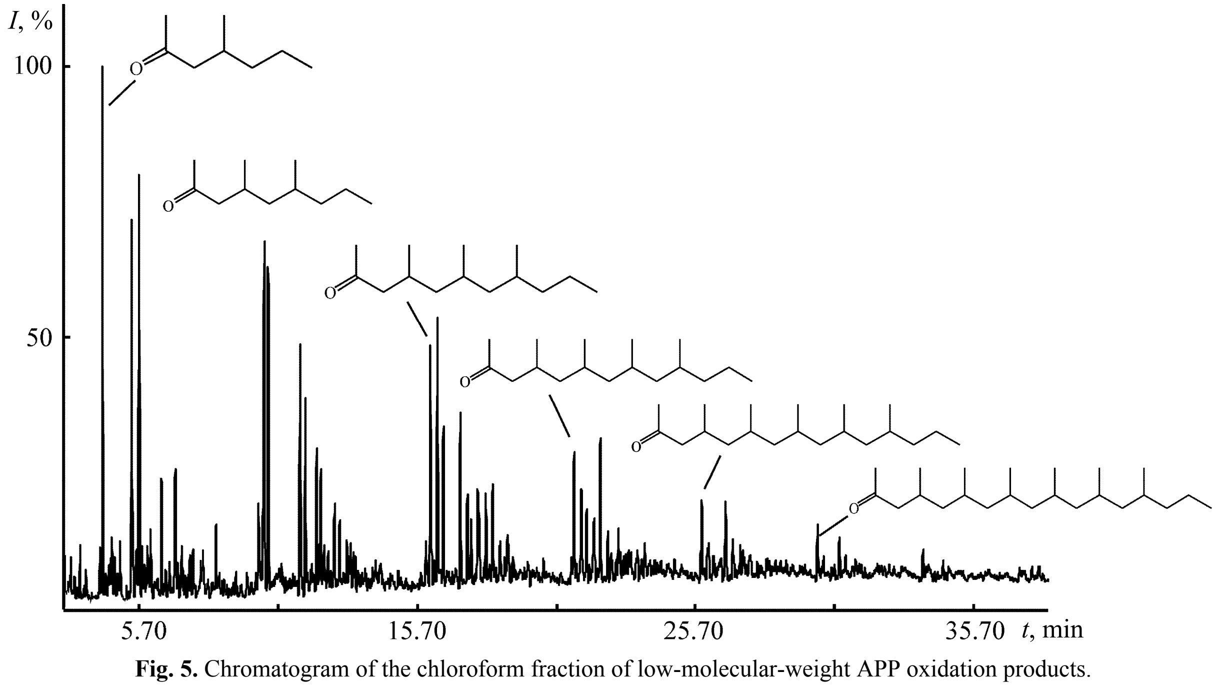


Fig. 5. Chromatogram of the chloroform fraction of low-molecular-weight APP oxidation products.

The chloroform–alcohol fraction (Fig. 7) contains unsaturated ketones, diketones, and hydroxy carboxylic acids.

Using the selective ion detection techniques, by the sum of the peak intensities *m*/*z* (60 + 73) we detected in this fraction a series of carboxylic acids, among which we identified isobutanoic, 2,4-dimethylpentanoic, and 2,4,6-trimethylheptanoic acids.

The general composition of the APP TOD products is given in the table. As can be seen, the low-mole-

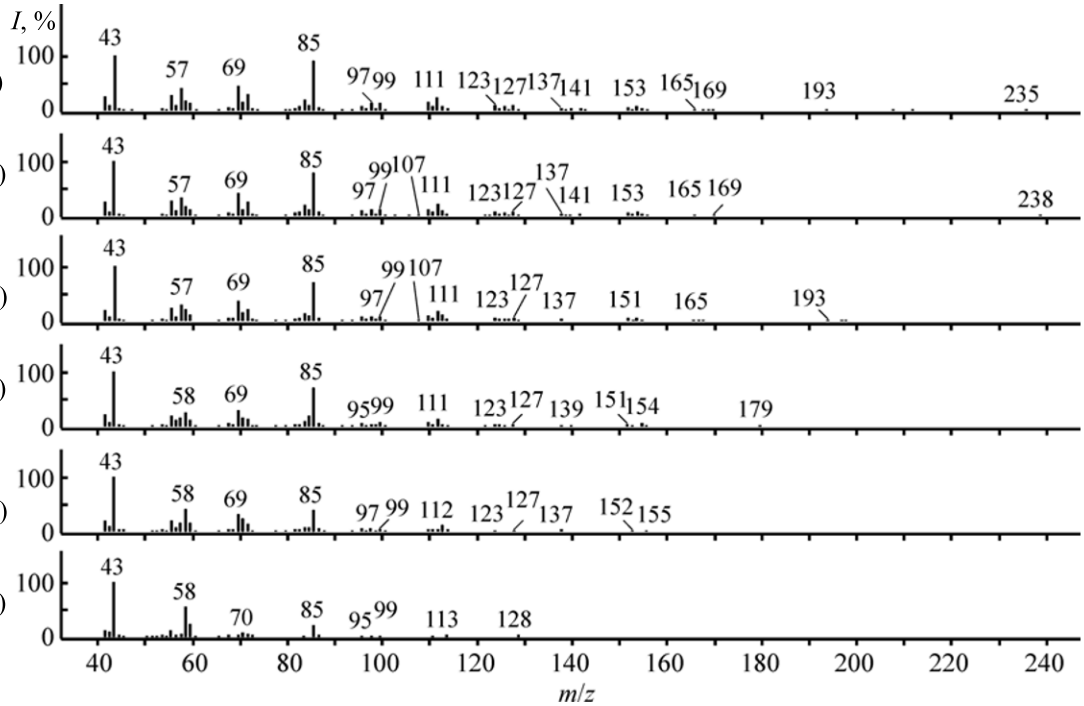


Fig. 6. Mass spectra corresponding to chromatographic peaks of ketones shown in Fig. 5. (a) $C_8H_{16}O$ (4.36 min), (b) $C_{11}H_{22}O$ (10.19 min), (c) $C_{14}H_{28}O$ (16.42 min), (d) $C_{17}H_{34}O$ (21.34 min), (e) $C_{20}H_{40}O$ (25.93 min), and (f) $C_{23}H_{46}O$ (30.09 min).

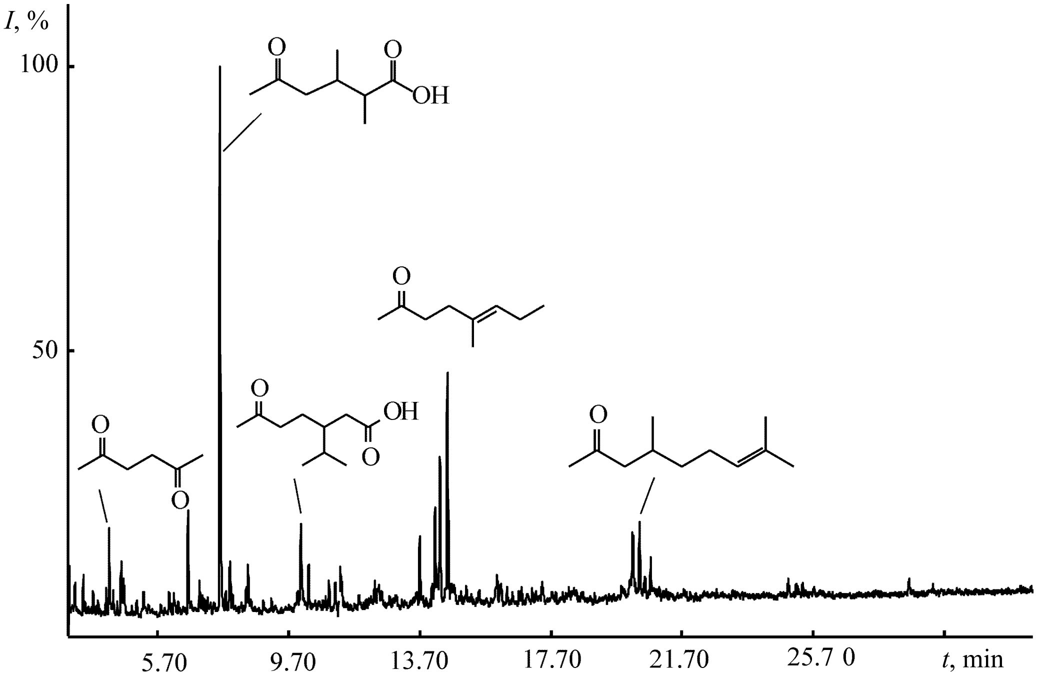


Fig. 7. Chromatogram of the chloroform–alcohol fraction of low-molecular-weight APP oxidation products.

cular-weight products mainly consist of saturated and unsaturated hydrocarbons. They also contain alcohols, ketones, esters, and carboxylic acids of various structures. Bernstein et al. [6] detected the same classes of compounds in low-molecular products of APP TOD.

The presence of oxygen-containing compounds opens prospects for using the low-molecular-weight oxidation products as modifying additives to hydrocarbon fuels, and the presence of carbonyl compounds allows these products to be recommended

Identified classes of compounds and their relative content in a mixture of low-molecular-weight products of APP oxidation

Class of organic compounds	Relative content, %			
	fraction			Sum of low-molecular-weight oxidation products
	hexane	chloroform	chloroform–alcohol	
Relative yield of fractions	98.38	1.51	0.11	100.00
Saturated hydrocarbons	81.39	6.40	–	80.17
Unsaturated hydrocarbons	16.95	1.16	–	16.70
Alcohols	1.11	29.93	25.51	1.57
Ketones	–	50.18	49.45	0.81
Carboxylic acids	–	–	13.21	0.015
Esters	–	–	4.86	0.005
Unidentified compounds	0.55	12.33	6.97	0.73

as plasticizers for thermoplastic sealing materials, because with an increase in the content of carbonyl groups the adhesive power of these products increases.

CONCLUSIONS

(1) The low-molecular-weight products of thermal oxidative degradation of atactic polypropylene mainly consist of saturated and unsaturated hydrocarbons, ketones, and alcohols of various structures.

(2) The low-molecular-weight oxidation products contain homologous series of compounds differing in the composition by one or several propylene groups.

(3) Higher polymethyl-substituted hydrocarbons of unique structure, promising for use in various branches of industry, were detected.

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