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MODIFICATION OF POLYMERS

Functionalization of Polyolefins via the Reaction of Ozone with Double Bonds

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Abstract—Polar groups are introduced into polyolefin chains via the postpolymerization polymer-analogous transformations using the ozonolysis of side ethylidene groups of ethylene (propylene) copolymers with the cyclic comonomer 5-ethylidene-2-norbornene. The copolymers are synthesized using *ansa*-zirconocene catalysts $Me_2Si[Ind]_2ZrCl_2$/MAO, $Et[Ind]_2ZrCl_2$/MAO and $Et[IndH_4]_2ZrCl_2$/MAO, which provide insersion of the cyclic monomer into the polymer chain without ring opening. The study of number-average molecular mass and compositions of homo- and copolymers of ethylene and propylene with 5-ethylidene-2-norbornene confirms a high selectivity of the ozonolysis of unsaturated double bonds of polyolefins. The formation of polar groups in the ozonized ethylene and propylene copolymers with 5-ethylidene-2-norbornene is proved by IR and Raman spectroscopy. The thermophysical characteristics of the initial and ozonized copolymers are compared.

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The design of polymers based on traditional polyolefins (POs) with a new complex of properties, such as increased adhesion, permeability, and improved colorability, is one of important practical problems currently existing in the field of olefin polymerization [1]. Polyolefins may be chemically modified by the introduction of polar groups into polyolefin chains by several methods, namely, the copolymerization of ethylene with a monomer containing polar groups [2–5], postpolymerization polymer-analogous transformations with participation of unsaturated end groups of polyolefn [6–9], and introduction into polyolefin macrochains of comonomer units containing groups with C=C double bonds that may be quantitatively transformed into polar groups [10–15].

Monofunctionalized polyolefins are synthesized using PE [9], atactic and *iso*-polypropylenes [6–8], poly(4-methyl-1-pentene) [8], and the copolymers of ethylene with propylene containing unsaturated end groups [8].

Polar groups may be also introduced into POs by the postpolymerization modification of ethylene and propylene copolymers with dienes [12, 13] and norbornene derivatives, such as 5-vinyl-2-norbornene (VN) [10–12] and 5-ethylidene-2-norbornene (EN) [14, 15]. The reactive C=C groups of these copolymers take the side position with respect to the main macrochain. The content of these groups in copolymers may be varied in a wide range by selecting the catalyst and copolymerization conditions. Using standard organic reactions (epoxidation, hydroboration, ozonolysis,

Table 1. Characteristics of polymer samples for ozonization of PE, PP, and their blends with ethylene, propylene, and EN copolymers

Sample	Composition	Content of C=C bonds, mol/g
1	PE with $M_w = 215000$	2.38×10^{-5}
2	16.6 wt % PE + 83.4 wt % ethylene–16 mol % EN	3.2×10^{-3}
3	Copolymer of ethylene and EN with 12.9 mol % EN	3.2×10^{-3}
4	Isotactic PP with $M_{C=C} = 81\,037$	2.35×10^{-5}
5	61.3 wt % *iso*-PP + 38.7 wt % propylene–34.4 mol % EN	1.09×10^{-3}
6	28.6 wt % *iso*-PP + 71.4 wt % propylene–22.2 mol % EN	4.0×10^{-3}
7	Copolymer of propylene and EN with 25.9 mol % EN	4.67×10^{-3}

Table 2. Molecular-mass characteristics of *iso*-PP synthesized with *ansa*-zirconocene catalysts which were measured by GPC and ozonization of end double bonds (polymerization conditions: 40°C, $[C_3H_6]$ = 0.26 mol/L, and 50 mL of toluene)

Catalyst			Molecular-mass characteristics of *iso*-PP				
ansa-zirconocenene–MAO	[Zr], μmol	molar ratio Al : Zr	$D_{C=C} \times 10^4$, mol/g	M_w, g/mol	M_w/M_n	M_n, g/mol	$M_{C=C}$, g/mol
rac-Et$[Ind]_2ZrCl_2$–MAO	107	1960	2,79	5300	1.7	3120	3580
rac-$Me_2C[Ind]_2ZrCl_2$–MAO	88	2560	2.51	5900	1.7	3930	3976
rac-Et$[Ind]_2ZrCl_2$–ZSM-5$(H_2O)AlMe_3$	1.3	4350	2.01	42950	8.8	4880	4910

iso-PP samples are fully soluble in CCl_4 at 0°C.

bromination, or chlorination), they may be quantitatively transformed into carbonyl, COOH–, borane, amino, and alcohol groups.

It is known that unsaturated low-molecular-mass and high-molecular-mass organic compounds can add ozone via the double bond in accordance with stoichiometry: one ozone molecule per one double bond. The reaction rate constant of ozone with double bonds is several orders of magnitude higher than the rate constants with other functional groups [16].

The purpose of the present work is to functionalize PE, PP, and ethylene and propylene copolymers with 5-ethylidene-2-norbornene via reaction with ozone and to investigate the structure and properties of polyolefin ozonization products.

EXPERIMENTAL

Polyolefins

In the present work, investigations were performed using PO samples, namely, polyethylene, isotactic polypropylene, and copolymers of ethylene (propylene) with 5-ethylidene-2-norbornene that were synthesized using metallocene catalysts based on *ansa*-zirconocene *rac*-Et$[Ind]_2ZrCl_2$, *rac*-Et$[H_4Ind]_2ZrCl_2$, and *rac*-$Me_2Si[Ind]_2ZrCl_2$ and cocatalyst methylaluminoxane (MAO) in toluene solution and the supported *rac*-Et$[Ind]_2ZrCl_2$/ZSM-5$(H_2O)AlMe_3$ catalyst. The technique of homopolymerization and copolymerization of olefins was described in [14].

Molecular-Mass Characteristics

The MMD of polypropylene samples was measured for 1,2,4-trichlorobenzene solutions at 140°C using a Waters-150 apparatus equipped with a differential viscometer. The universal polystyrene calibration was used to determine molecular mass values.

Determination of Composition of Ethylene (Propylene) Copolymers with EN

The content of EN in the copolymer was calculated from the yield of copolymerization products and the consumption of ethylene (propylene) in copolymerization [14] and was also determined by the ozonization of end and side double bonds C=C of copolymers [16, 17]. The ozonization method used has a high threshold sensitivity (10–11 moles of C=C bonds), ±1% accuracy, and a speed of 0.5–5.0 min per measurement.

Functionalization of Polyolefins

The polymer (copolymer) solution in an organic solvent (carbon tetrachloride or *o*-dichlorobenzene) with a concentration of 1.5–2.5 g/L was placed in a reactor, through which an ozone-oxygen mixture was bubbled at 0°C with the ozone concentration not exceeding 1×10^{-6} mol/L. The ozonization of finely dispersed polymer powders with an average particle size of 0.1–0.3 μm was carried out in a fluidized bed at room temperature. The ozone adsorption in the reaction with PO double bonds was measured using an ADS-5 instrument for analysis of double bonds [17] as described in [18, 19].

Investigation of the Structure and Properties of Polymers

To compare the structure and properties of the synthesized POs and the ozonized polymers, their IR spectra (Bruker Tensor-27FTIR) and Raman spectra (PerkinElmer Raman Station 400) were taken. The thermophysical characteristics of the samples (T_m, T_g, degree of crystallinity) were measured. The DSC curves were measured on a Netzsch DSC-204 F1 scanning calorimeter (Germany) in the temperature range of 20–160°C at 10 K/min heating in a flow of inert argon gas. The accuracy of temperature measurements was 0.1°C.

Table 3. Content of EN and unsaturated C=C bonds in copolymers with ethylene and propylene obtained using homogeneous *ansa*-zirconocene catalysts (copolymerization conditions: 40°C, $[C_2H_4] = 0.057$ mol/L, and $[C_3H_6] = 0.260$ mol/L)

Olefin	Catalyst	[Zr], μmol	Molar ratio Al : Zr	Molar ratio $[EN]_0$: $[olefin]_0$	$[EN] \times 10^3$ in polymer product, mol/g	$[C{=}C] \times 10^3$ in copolymer, mol/g
Ethylene	*rac*-Et$[Ind]_2ZrCl_2$–MAO	12.20	1000	6.5	2.56	2.62
		6.40	1875	8.6	5.27	5.50
		8.60	1480	16.1	6.16	6.02
	rac-Et$[H_4Ind]_2ZrCl_2$–MAO	5.80	1800	11.75	6.95	6.75
		4.90	2230	2.20	2.56	2.79
	rac-$Me_2Si[Ind]_2ZrCl_2$–MAO	5.13	2030	4.38	4.26	4.38
		1.33	2820	10.43	6.00	6.70
Propylene	*rac*-Et$[Ind]_2ZrCl_2$–MAO	4.50	1700	1.56	6.20	5.70
70 wt % *iso*-PP–30 wt % propylene–EN copolymer	*rac*-Et$[Ind]_2ZrCl_2$–MAO	4.30	1700	1.65	0.75	0.82
65 wt % *iso*-PP–35 wt % propylene–EN copolymer	*rac*-Et$[Ind]_2ZrCl_2$–MAO	19.00	3500	1.8	4.2	4.0

Table 4. DSC study of initial and ozonized polymers, *iso*-PP, and *iso*-PP blends with propylene–EN copolymer

Test	Composition of the sample for ozonization	Sample	DSC (first melting)			DSC (second melting)		
			T_m, °C	ΔH, J/g	λ*, %	T_m, °C	ΔH, J/g	λ, %
4	*iso*-PP	Initial	132	67.94	41.1	131	65.18	39.5
		Ozonized	128	61.36	37.2	131	67.41	40.8
6	*iso*-PP + propylene–EN copolymer	Initial	122.4	49.3	29.9	121	53.52	32.4
		Ozonized	121	95.59	57.9	119	66.1	40.0

*Crystallinity calculated with allowance for the ΔH of isotactic PP monocrystal which is 165 J/g [23, 24].

RESULTS AND DISCUSSION

The PO samples used in ozonization were synthesized by the polymerizations of ethylene and propylene and the copolymerization of ethylene (propylene) with cyclic EN comonomer and by the two-stage homopolymerization of ethylene (propylene) followed by their copolymerization with EN. The data on the composition, molecular-mass and thermophysical characteristics of the synthesized polymer products, and the content of groups containing C=C bonds are summarized in Tables 1–4.

Figures 1 and 2 show the curves illustrating the consumption of ethylene and propylene in one- or two-stage homo- and copolymerization of olefins with EN. The two-stage processes consisting of the polymerization of ethylene or propylene followed by their copolymerization with higher or cyclic olefins are an effective method of producing reactor polymer blends. These processes are similar to the industrial processes based on the multireactor scheme [20]. The compositions of the copolymers formed by one-stage copolymerization and postpolymerization are the same [21, 22].

According to the kinetic data obtained, the introduction of EN into the polyolefin polymer in postcopolymerization is more preferable than in one-stage copolymerization of ethylene (propylene) with the EN monomer. The reason is that the reactivities of linear and cyclic olefin comonomers in copolymerization with metallocene catalysts are different (r_{Et}. in ethylene copolymerization with EN is 10–7 [25], and r_{Pr} in propylene copolymerization with VN is >1 [11]). Moreover, this phenomenon may be connected with an increase in the number of the most active sites initiated by ethylene (or propylene) in the homopolymerization of the linear olefins compared with their number in copolymerization with EN [25]. The total yield of PO and of olefin–EN copolymer blend is higher than the yield of copolymers in one-stage copolymerization. In this case, the contents of C=C bonds in the polymer products are similar (Table 1, samples 2 and 3 and 6 and 7).

A high selectivity of the ozonization of unsaturated double bonds in the structure of olefin homo- and copolymers is confirmed by the GPC study of the number-average molecular mass of POs and $M_{C=C}$

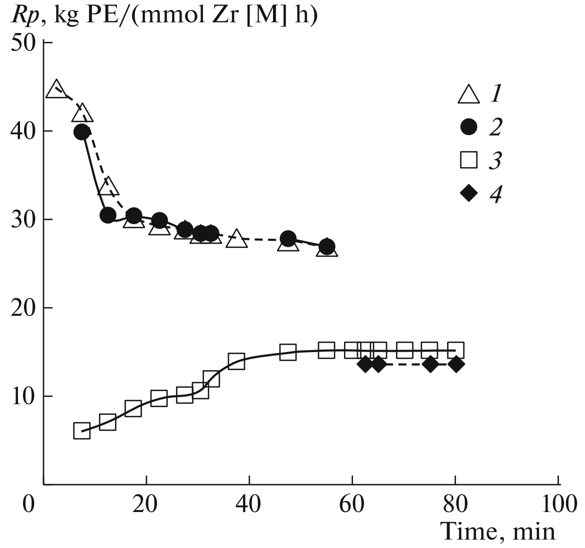


Fig. 1. Kinetic curves of (*1, 2*) ethylene polymerization and (*3*) ethylene–EN copolymerization, and (*4*) ethylene–EN copolymerization after homopolymerization of ethylene using the Et[Ind]$_2$ZrCl$_2$–MAO catalyst at $T = 40°\mathrm{C}$. [Zr]: (*1*) 3.28 and (*2–4*) 1.67 μmol. Al : Zr molar ratios: (*1*) 1080, (*2, 4*) 3000, and (*3*) 2560; ethylene concentrations are (*1*) 0.03 and (*2–4*) 0.057 mol/L; (*3, 4*) EN : ethylene initial molar ratios are 2.16.

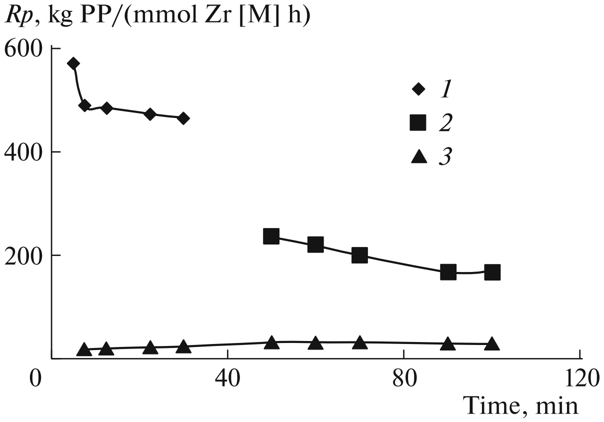


Fig. 2. Kinetic curves of (*1*) propylene polymerization, (2) propylene–EN copolymerization after homopolymerization of propylene, and (*3*) propylene–EN copolymerization using the Et[Ind]$_2$ZrCl$_2$–MAO catalyst at $T = 40°\mathrm{C}$. [Zr]: (*1, 2*) 19 and (*3*) 31.6 μmol. Al : Zr molar ratios: (*1, 2*) 360 and (*3*) 220; propylene concentrations is 0.287 mol/L; (*2, 3*) initial EN : ethylene molar ratios are 1.80.

values, which were calculated from composition of ethylene (propylene)–EN copolymers using the kinetic data and from the content of side ethylidene groups as found by ozonolysis.

In the polymerization of olefins with metallocene catalysts, the main reactions controlling polymer chain length are the reaction of chain transfer to metal (Zr, Hf) (**1**) and coordinated monomer (**2**) via β elimination; under certain conditions chain transfer to organoaluminum cocatalyst may occur (**3**):

$$\begin{gathered}\mathrm{MtCH_2{-}CHR{-}[CH_2{-}CHR]_n{-}CH_2{-}CH_2R}\\ \rightarrow \mathrm{CH_2{=}CR{-}[CH_2{-}CHR]_n{-}CH_2{-}CH_2R + MtH},\end{gathered} \tag{1}$$

$$\begin{gathered}\mathrm{MtCH_2{-}CHR{-}[CH_2{-}CHR]_n{-}CH_2{-}CH_2R}\\ \mathrm{+\ CH_2 = CHR} \rightarrow \mathrm{CH_2}\\ \mathrm{={CR}{-}[CH_2{-}CHR]_n{-}CH_2{-}CH_2R}\\ \mathrm{+MtCH_2{-}CH_2R},\end{gathered} \tag{2}$$

$$\begin{gathered}\mathrm{MtCH_2{-}CHR{-}[CH_2{-}CHR]_n{-}CH_2{-}CH_2R}\\ \mathrm{+\ AlR'_3} \rightarrow \mathrm{AlR'_2CH_2{-}CH(CH_3){-}[CH_2{-}CHR]_n}\\ \mathrm{{-}CH_2{-}CH_2R + MtR'},\end{gathered} \tag{3}$$

where $\mathrm{R = H}$ or $\mathrm{CH_3}$, and $\mathrm{R' = Et}$ or Cl.

Depending on the origin of the catalyst, the reactions of β-hydride elimination (1) and chain transfer to monomer (2) and to organoaluminum cocatalyst (3) predominate among the reactions of chain propagation termination in olefin polymerization. The first two reactions lead to formation of a polymer molecule with end double bonds (vinyl bond in ethylene polymerization and vinylidene bond in propylene polymerization). Using the concentration of end double bonds in the polymer product, which is determined by ozonization, the number-average MM of the polymer may be determined as $M_{\mathrm{C=C}}$ (g/mol) = $1/\mathrm{D_{C=C}}$ ($\mathrm{D_{C=C}}$ is the degree of unsaturation, mol C=C/g). Table 2 shows the molecular-mass characteristics of *iso*-PP, which was synthesized with *ansa*-zirconocene catalysts. The data were obtained by GPC and ozonization of PP end double bonds. According to these results, the number-average molecular masses of *iso*-PP samples which were determined by GPC and ozonization are similar. This means that each polymer chain reacting with ozone contains one end double bond.

Polar groups were introduced into the structure of polyolefin chains by postpolymerization polymer-analogous transformations using the copolymers of ethylene and EN containing 10–65 mol % EN and propylene and EN from 25 to 60 mol % in the reaction with ozone. As was shown in [14], in the copolymerization of EN with olefins, the regioselective insertion of the cyclic monomer into the main polymer chain occurs via the endocyclic double bond; its side double bond is not involved in copolymerization [14]. As a result, each EN unit of the copolymer macrochain contains ethylidene group $\mathrm{C{=}CH{-}CH_3}$. The content of double bonds in these copolymers was measured. A comparison of data on the ozonolysis of the copolymers with the data on the copolymer composition which were calculated from the yield of copolymer products and the consumption of olefins made it possible to state that the copolymerization of ethylene (propylene) with EN in the presence of metallocene catalysts leads to formation of copolymers in which

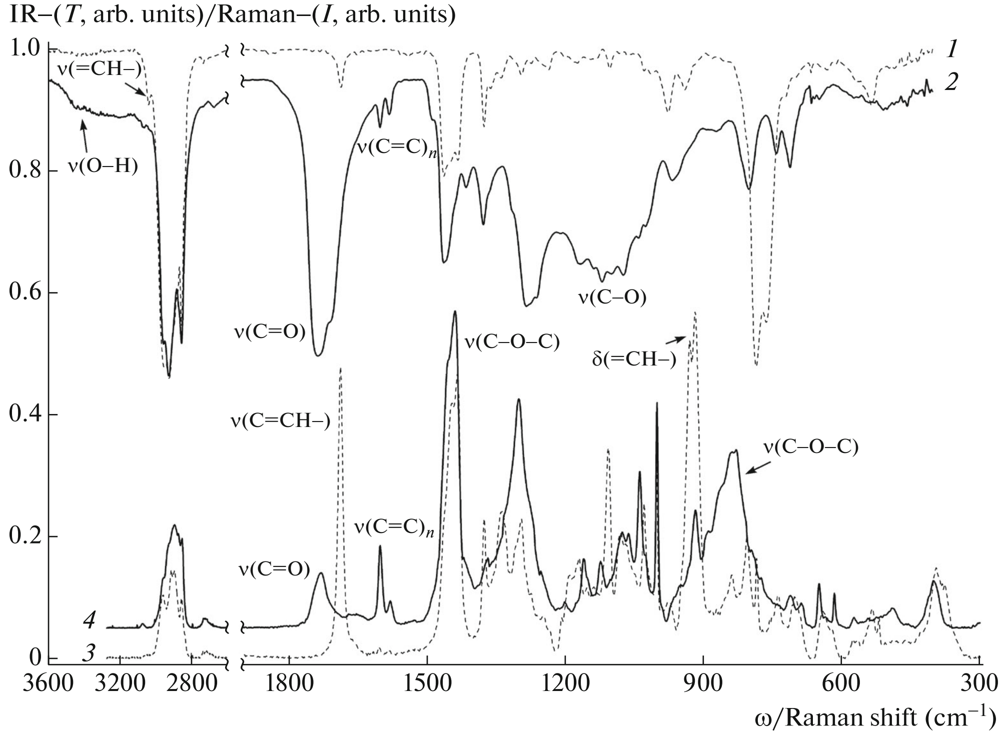
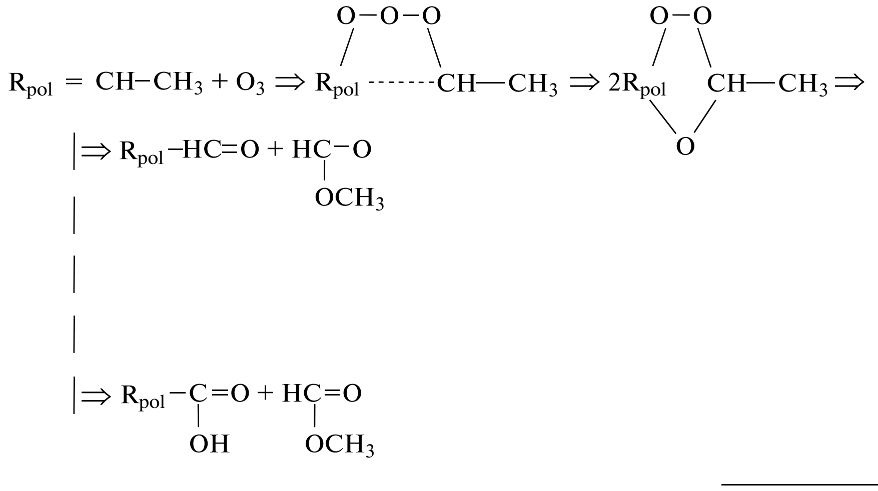


Fig. 3. (*1, 2*) IR and (*3, 4*) Raman spectra of ethylene–EN copolymer (*1, 3*) before and (*2, 4*) after ozonization.

each unit of the cyclic comonomer contain the side ethylidene group (Table 3).

The structure of the initial and ozonized ethylene–EN copolymers (Fig. 3) and the propylene–EN copolymer and PP blend (Fig. 4) was studied using IR and Raman spectroscopy. It was shown that, in the IR spectra of the ozonized copolymers, absorption bands characteristic of ethylidene groups (3038, 1655 + 1689, and 765 + 787 cm^{-1} [26–30]) disappear, while 1700–1725, 1740, and 1750 cm^{-1} bands appear. These bands correspond to vibrations of carboxyl, aldehyde, and ketone groups; a number of absorption bands observed at 1150–1040 cm^{-1} may be attributed to the stretching vibrations of C–O and C–O–C groups [29]. These results correlate with the scheme including the sequential reactions of formation and decomposition of ozonides [18, 19]:



In addition, note that, in the Raman spectra of the ozonized ethylene–EN and propylene–EN copolymers, a well-defined band near 1600 cm^{-1} is registered; this band may be attributed solely to vibrations of two or more conjugated C=C bonds [29, 30]. The optical microscopy of the ozonized copolymers shows

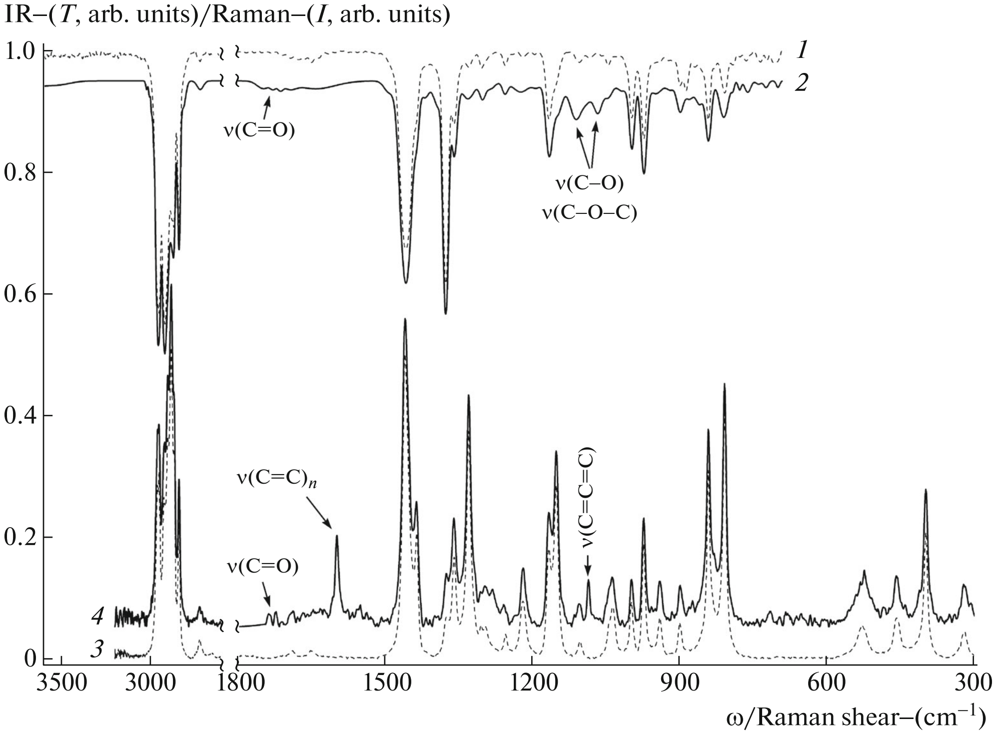


Fig. 4. (*1, 2*) IR and (*3, 4*) Raman spectra of propylene–EN copolymer blend with *iso*-PP (*1, 3*) before and (*2, 4*) after ozonization. Blend composition: 71.4 wt % copolymer and 28.6 wt % *iso*-PP; the EN content in the copolymer is 22 mol %.

microscopic red inclusions that may provide additional evidence for the presence of conjugated double bonds as well as the fact that the ethylene–EN copolymer (with a high EN content) (Fig. 3) is subjected to deeper transformations of the molecular structure during ozonization than the blend of propylene–EN copolymer with PP (with a substantially lower EN content (Fig. 4)). In fact, the blend of propylene–EN with PP preserves all attributes of the molecular structure characteristic of IR and Raman spectra of polypropylene after ozonization.

The properties of the initial and ozonized samples of *iso*-PP, *iso*-PP + propylene–EN (Table 4), and propylene copolymer with EN were compared. According to the DSC data, the introduction of polar groups into polyolefin insignificantly affects their thermophysical characteristics. A slight decrease in T_m (by no more than 2°C) and a slight increase in the degree of polymer crystallinity (after 1.5% ozonization of *iso*-PP, the degree of crystallinity of the blend with propylene–ethylene copolymer is less than 10%) are observed. The T_g of the copolymers changes slightly; namely, after ozonization, the T_g of the propylene–EN copolymer containing 25.9 mol % EN increases from 50.7 to 52.5°C.

Thus, our data have confirmed that the use of the ozonolysis reaction in the postpolymerization polymer-analogous transformations of olefin copolymers with substituted norbornenes is one of the ways to produce polymers containing polar groups. The main polyolefin chain of PE and PP may be functionalized by one- or two-stage homo- and copolymerization of ethylene (propylene) and cyclic comonomer EN followed the ozonolysis of side ethylidene groups. The high selectivity of ozonolysis of unsaturated double bonds in olefin homo- and copolymers provides the introduction of polar groups into the polyolefin macrochain without its degradation.

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