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Polyolefins functionalization by copolymerization of ethylene (propylene) with substituted norbornene

Summary — A number of new copolymers of ethylene (propylene) and 5-ethylidene-2-norbornene (EN) containing 5—62 mol. % of the cyclic comonomer units in the main chain have been synthesized by employing of three *ansa*-metallocene catalytic systems, namely: $Et[Ind]_2ZrCl_2$/methylalumoxane, $Et[IndH_4]_2ZrCl_2$/methylalumoxane or $Me_2Si[Ind]_2ZrCl_2$/methylalumoxane. In this way side $>C=CH-CH_3$ groups in the range up to $7 \cdot 10^{-3}$ mol/g were incorporated into a structure of polyolefin chain. As it was found by IR-spectroscopy, the side ethylidene groups of poly(ethylene-*co*-5-ethylidene-2-norbornene) were susceptible to ozonolysis reactions and converted into the polar carbonylic groups. According to DSC, X-ray diffraction and very cold neutrons scattering (VCN) data, enrichment of poly(ethylene-*co*-5-ethylidene-2-norbornene) with EN units has lead to eventual transformation of the studied copolymers from a partly crystalline state to a fully amorphous one. With the growing cyclic comonomer partial content the copolymers have exhibited progressively better optical transparency and higher glass transition temperatures (up to 85 °C); they are characterized by a high density ($d > 1000$ kg/m^3).

Key words: metallocene catalysts, olefins, 5-ethylidene-2-norbornene, copolymerization, supramolecular structure, chemical structure, thermal properties, transparency.

FUNKCJONALIZACJA POLIOLEFIN W WYNIKU KOPOLIMERYZACJI ETYLENU (PROPYLENU) Z PODSTAWIONYM NORBORNENEM

Streszczenie — Z udziałem trzech katalizatorów metalocenowych, mianowicie układów $Et[Ind]_2ZrCl_2$/MAO, $Et[IndH_4]_2ZrCl_2$/MAO, $Me_2Si[Ind]_2ZrCl_2$/MAO (MAO = metyloalumoksan), otrzymano szereg nowych kopolimerów etylenu (propylenu) z 5-etylideno-2-norbornenem (EN), zawierających 5—62 % mol. tego cyklicznego komonomeru w łańcuchu polimerowym (tabela 1). W ten sposób wprowadzono do struktury łańcucha poliolefinowego boczne grupy $>C=CH-CH_3$ w ilości $1 \cdot 10^{-3}$—$7 \cdot 10^{-3}$ mol/g kopolimeru (tabela 2). Potwierdzona metodą spektroskopową IR obecność bocznych grup etylidenowych w kopolimerach etylen/EN pozwala na przeprowadzenie reakcji ozonolizy powodującej utworzenie polarnych grup karbonylowych w polimerze. Z badań otrzymanych kopolimerów metodami DSC, XRD (rys. 2 i 3) i VCN (rozpraszanie bardzo zimnych neutronów) wynika, iż wzrost udziału cyklicznych jednostek 5-etylideno-2-norbornenu w kopolimerze prowadzi do jego transformacji z polimeru częściowo krystalicznego do całkowicie amorficznego (tabela 4—6). Powoduje to także, iż kopolimer staje się bardziej przezroczysty (rys. 4) oraz charakteryzuje się podwyższoną (do 85 °C) temperaturą zeszklenia i zwiększoną gęstością (przekraczającą 1000 kg/m^3, rys. 1).

Słowa kluczowe: katalizatory metalocenowe, olefiny, 5-etylideno-2-norbornen, kopolimeryzacja, struktura supramolekularna, budowa chemiczna, właściwości cieplne, przezroczystość.

Commodity polyolefins, although characterized with a lot of practically valuable properties, usually do not contain polar groups in their macromolecules and hence exhibit low adhesion and poor antistatic characteristics which may be the limiting factors in many important applications. To enhance their ability to interact with foreign materials, the homopolyolefins are modified by preparation of corresponding functionalized block- or graft-*co*-polyolefins. Embedding into a polyolefin chain such polar segments or blocks as poly(methyl methacry-

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late), poly(winyl acetate) or polycaprolactone [1] let to enhance the polyolefin adhesion to glass and metals [2, 3]. The modified polyolefins are suitable for coloring with dye-stuffs and can be used as substrates for printing [4].

Up to date, the production of functionalized block-*co*-polyolefins by polymerization has been rather problematic. For traditional Ziegler—Natta catalysts, the rate of olefins' copolymerization with the polar comonomers is usually low due to poisoning of the active centers of catalyst by the polar comonomer or due to the low copolymerization activity of the last one. Zirconocene catalysts are considered to be the most efficient ones for preparation of polyolefins containing polar groups. Currently, there are two main routes to obtain the functionalized polyolefins by the catalytic polymerization. According to the first, incorporation of polar groups into a polyolefin macromolecule is accomplished by means of one-step copolymerization of an olefin with a polar comonomer [5—8]. According to the other, the reaction is carried out by use of a comonomer containing a latent reactive group capable to give the required functionalized polyolefin later by virtue of subsequent polymer-analog transformations [9].

The goal of this work was to incorporate the functional side $C=CH-CH_3$ groups into polyethylene or polypropylene by copolymerization of olefin with 5-ethylidene-2-norbornene (EN) in the presence of *ansa*-metallocene/methylalumoxane (MAO) catalysts, to receive the polymer materials combining high glass transition temperature, high density, transparency and ability for post-polymerization polymer-analog transformations. With *ansa*-zirconocene catalysts [$Et(Ind)_2ZrCl_2$/MAO, $Et(IndH_4)_2ZrCl_2$/MAO and $Me_2Si(Ind)_2ZrCl_2$/MAO] (Ind = indenyl) the ethylene/EN and propylene/EN copolymers with different contents of EN and the reactive side $>C=CH-CH_3$ groups in the copolymer chains were synthesized. Thus prepared copolymers have been investigated in terms of their morphological, thermophysical and optical properties. Postpolymerization modification of ethylene/EN copolymers has been studied by means of ozonization of the $>C=CH-CH_3$ groups pendant at EN units of the main chain.

EXPERIMENTAL

Materials

$Et(Ind)_2ZrCl_2$, $Et(IndH_4)_2ZrCl_2$, $Me_2Si(Ind)_2ZrCl_2$ (Aldrich Co.) and methylalumoxane (Aldrich Co., 10 wt. % in toluene) were used as received.

5-ethylidene-2-norbornene (Aldrich Co.) was purified by refluxing over sodium wire, subsequent distillation under vacuum and stored in nitrogen atmosphere.

The spectral-grade toluene (Aldrich Co.) was purified in the same way as EN.

Ethylene and propylene were polymerization-grade.

Copolymerization procedure

The formation of catalytic complex and a following olefin copolymerization were carried out in 0.5 dm^3 glass reactor equipped with units for feeding of solvent, catalyst and comonomers and stirrer as well. The reagents (toluene, MAO, zirconocene and EN) were introduced into the reactor at room temperature. After heating of the reaction mixture up to the copolymerization temperature the reaction zone was saturated by ethylene (propylene). The saturation time was 1.5—2 minutes for ethylene and 3—5 minutes for propylene. During copolymerization the ethylene (propylene) pressure, the temperature and the stirring rate of reaction mixture were maintained constant.

The ethylene copolymerization conditions were as follows: temperature 40 °C, pressure 0.2—0.5 bar, the initial EN/ethylene molar ratio varied from 2 to 10, for propylene it was 1.6. Zirconocene concentration was changed in the range of $1 \cdot 10^{-5}$— $11.5 \cdot 10^{-5}$ mol/dm^3, molar ratio Al/Zr — from 1700 to 2800. The conditions for propylene homo- and copolymerization are given in Table 1, runs 15 and 16.

The catalytic activity (A) and the rate of the ethylene (propylene) incorporation into copolymer chain were calculated from their consumption during the process. The content of EN in the obtained copolymer sample was determined from the copolymer product yield and the ethylene (propylene) consumption, as well as by ozonization of the side double bonds of copolymer chain [10]. A method is found on ability of the unsaturated compound to add ozone (one O_3 molecule to one C=C bond) with high rate — the rate constant $k = 10^5$ l/(mol · s).

Ethylene homo- and copolymers characterization

IR-spectra of copolymers were obtained using Perkin-Elmer FTIR-1720 apparatus.

The density of synthesized samples of homopolymers and copolymers of ethylene with EN was determined by the flotation method (ASTM D 1505) at 20 °C using an ethanol/water mixture as a working fluid. The measurement accuracy was up to ± 0.1 %.

X-ray studies of the melt molded EN/ethylene copolymer samples with different contents of EN were performed using a DRON-2.0 general-purpose diffractometer (CuKα radiation, 20 mA, 40 kV, 14°—28° range). The degree of crystallinity of copolymer samples (χ) was estimated according to the standard Hermans—Weidinger method [11], which was modified as described in [12]. The size of the copolymer crystallites (L) was determined from the half-width of reflections [110] and [200], and calculated by the Scherrer formula [13]. As a reference, we used a [200] line of graphite having a reflection at an angle $2\theta = 24.8°$ close to the angles of reflections of copolymers under examination.

The supramolecular structure of the EN/ethylene copolymers was tested also using the original technique of very cold neutron (VCN) scattering developed at the Lebedev Physical Institute of the Russian Academy of Sciences [14—16]. Neutron wavelengths lie in the range 1—100 nm and neutrons energies — in the range $2 \cdot 10^{-7}$—$5 \cdot 10^{-4}$ eV. In order of magnitude, the values of wavelength coincide with the characteristic sizes of the supramolecular structures of the polymers. The VCN scattering experimental (determinations of sizes and concentrations of scattering particles) were performed using a time-of-flight spectrometer in the wavelength range 4 nm < λ < 60 nm. The measurements were conducted at 300 K using copolymer sample (thickness 150—250 μm) and measured surface area 2.5 × 3.5 cm^2.

T a b l e 1. Effects of the catalyst nature and conditions of the homo-[a] and copolymerization of ethylene (runs 1—14) or propylene (runs 15, 16) with EN on the activity of *ansa*-zirconocene catalysts and the copolymers composition

No.	Catalyst	The initial EN/ethylene (EN/propylene) molar ratio	[Zr] mmol/l	Al/Zr molar ratio	T_{pol}[b] °C	t_{pol}[c] min	Yield g	Conversion of EN, %	A[d]	[EN] in copolymer mol. %
1	Et[Ind]$_2$ZrCl$_2$/MAO	—	0.065	3150	33	60	0.60	—	15 000	0
2	Et[Ind]$_2$ZrCl$_2$/MAO	2.0	0.026	2550	40	60	4.60	100.0	14 600	5.3
3	Et[Ind]$_2$ZrCl$_2$/MAO	8.6	0.106	1875	40	85	5.64	100.0	2800	28.0
4	Et[Ind]$_2$ZrCl$_2$/MAO	7.7	0.035	2510	40	160	1.29	24.0	1645	30.0
5	Et[Ind]$_2$ZrCl$_2$/MAO	22.5	0.115	1850	40	180	0.98	8.5	1000	43.0
6	Et[Ind]$_2$ZrCl$_2$/MAO	—	3.6	120	40	300	0.25	3.5	—	100.0
7	Et[IndH$_4$]$_2$ZrCl$_2$/MAO	—	0.023	4160	40	90	2.00	—	10 400	0
8	Et[IndH$_4$]$_2$ZrCl$_2$/MAO	11.8	0.060	1800	40	190	1.89	24.0	1170	62.0
9	Et[IndH$_4$]$_2$ZrCl$_2$/MAO	—	0.112	2660	42	450	0.04	—	—	100.0
10	Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO	—	0.132	1370	40	65	4.2	—	5800	0
11	Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO	2.2	0.084	2230	40	50	2.9	100.0	4870	9.4
12	Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO	4.4	0.087	2030	40	100	4.7	100.0	1900	20.0
13	Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO	6.5	0.083	2010	40	290	3.0	37.0	1000	31.0
14	Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO	10.4	0.020	2800	40	170	0.4	23.8	800	37.0
15	Et[Ind]$_2$ZrCl$_2$/MAO	—	0.010	1700	40	20	1.0	—	3000	0
16	Et[Ind]$_2$ZrCl$_2$/MAO	1.6	0.010	1700	40	190	1.0	100.0	120	50.0

[a] Concentration of monomers in homopolymerization: — ethylene concentration in run 1 is 0.024 mol/l, in the runs 7 and 10 — 0.058 mol/l; — EN concentration in runs 6 and 9 is 0.99 and 0.47 mol/l, respectively; — propylene concentration is 0.26 mol/l in the run 15; volume of toluene 80 ml.

[b] T_{pol} = Polymerization temperature.

[c] t_{pol} = Polymerization time.

[d] A — catalyst activity: A for ethylene consumption in homo- and copolymerization with EN, kg PE/(mol Zr · mol C_2H_4 · h), runs 1—14; A for propylene consumption in homo- and copolymerization with EN, kg PP/(mol Zr · mol C_3H_6 · h), runs 15 and 16.

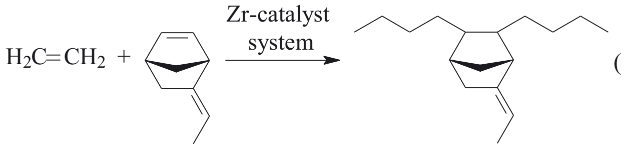
The transparency of EN/ethylene copolymers in near UV and visible range spectrum (in the range λ = 200—750 nm) was investigated using an instrument "Specol UV-vis" (the spectral permission was 2 nm).

Calorimetric analyses (T_m, ΔH and T_g of the copolymer products) were carried out using a Perkin-Elmer DSC-7 calorimeter. The DSC curves were recorded at a heating rate 10 K/min.

RESULTS AND DISCUSSION

Copolymerization, catalyst activity, monomers reactivity ratios and general characterization of obtained products

As we mentioned previously, copolymerization of ethylene and EN was catalyzed by three *ansa*-zirconocene systems: Et[Ind]$_2$ZrCl$_2$/MAO, Et[IndH$_4$]$_2$ZrCl$_2$/MAO or Si[Ind]$_2$ZrCl$_2$/MAO. Similarly to copolymerization of ethylene [9] or propylene [17] with 5-vinyl-2-norbornene, the copolymerization of ethylene and EN proceeds by virtue of regioselective insertion of an endocyclic double bond of the cyclic comonomer into the main chain, the ethylidene double bond of EN remaining intact:



(1)

FTIR spectra of the ethylene/EN copolymers have revealed absorption bands at 3038, 1687 and 808 cm^{-1}, which are characteristic for the ethylidene unsaturation [18, 19]. Any absorption in the vicinity of 712 cm^{-1} which is normally assignable to the endocyclic double bond of EN monomer molecule was absent in the spectra of copolymers.

T a b l e 2. Contents of EN and C=C in ethylene/EN and propylene/EN copolymers

No. (see Table 1)	[EN] in copolymer mol/g	[C=C] in copolymer mol/g
12	0.0042	0.0044
4	0.0057	0.0050
13	0.0063	0.0055
8	0.0069	0.0067
16	0.0062	0.0057

Calculated compositions of the prepared ethylene/EN copolymers (from the ethylene consumption and yield of copolymer product — Table 1) have shown a good correlation with the results of ozonization of ethylidene double bonds (Table 2), proving that the *ansa*-zirconocene catalysts systems used by us do give copolymers in which every cyclic comonomer unit bears the pendant unsaturated group.

Among the three catalytic systems studied in this work, that one based on Et(Ind)$_2$ZrCl$_2$ appeared to be the most active in both ethylene homo- and copolymerization with EN. This catalyst has provided higher consumption of C_2H_4 during these processes (Table 1, *A* values) as well as accelerated ethylene incorporation to copolymer chain.

The contents of EN units in the prepared ethylene/EN copolymers varied in the range of 5.3—62 mol. %, while the content of EN units in the propylene/EN copolymers was 50 mol. %. Based on the composition data for ethylene/EN copolymers prepared in the runs with the cyclic comonomer conversions not exceeding 25 mol. %, both monomers reactivity ratios (r_1, r_2) have been evaluated by Fineman—Ross method. For copolymerizations in the presence of Et[Ind]$_2$ZrCl$_2$/MAO system, the values of r_1 = 10.5 and r_2 = 0.004 have been found for ethylene and EN, respectively, whereas for Si[Ind]$_2$ZrCl$_2$/MAO system, the values of r_1 = 8.7 and r_2 = 0.007 have been obtained. The found copolymerization constants' values show that in the presence of the *ansa*-zirconocene catalysts, EN monomer is less readily introduced into the copolymer chain as compared with unsubstituted norbornene.

The values of r_1 found in this work appeared to be higher, while the values of r_2, lower than those known from literature on the copolymerization of ethylene and norbornene [20—23]. Contrary to copolymerization of ethylene and unsubstituted norbornene [24], the sterical volume and flexibility of the bridge in the *ansa*-zirconocene catalyst ligand have no pronounced effects on EN monomer capability to incorporate into the copolymer chain. By increasing EN concentration within the reaction zone (using higher [EN]/[ethylene] molar ratio), the copolymers were enriched with the cyclic comonomer units and showed lower molecular weights (based on intrinsic viscosity measurements' data) (Table 3).

T a b l e 3. Influence of EN content on intrinsic viscosity ([η]) of ethylene/EN copolymers obtained in the presence of Et[Ind]$_2$ZrCl$_2$/MAO catalyst[a]

EN:ethylene molar ratio	[Zr] mol/l	Al:Zr molar ratio	T_{pol} °C	[EN] in copolymer mol. %	[η] dl/g[b]
—	0.065	3150	33	0	2.30[c]
8.6	0.106	1850	40	28.6	0.25
16.0	0.143	1480	40	30.5	0.18
22.6	0.115	1840	40	43.0	0.15

[a] Ethylene concentration in homopolymerization — 0.024 mol/l, in copolymerization with EN — 0.057 mol/l.
[b] 135 °C, in decalin.
[c] From GPC data M_w of PE = 258 500 and M_n = 84 000.

Density of a polymer product, being one of the most important parameters determining the properties of homo- and copolymers, is dependent on the polymer composition and the conditions of its preparation (comonomers ratio, catalytic system used, *etc*.). Figure 1 shows density data measured experimentally for the hot-pressed samples of homo-PE and ethylene/EN copolymers prepared in the presence of Et[Ind]$_2$ZrCl$_2$/MAO or Si[Ind]$_2$ZrCl$_2$/MAO catalysts. The studied catalysts let obtain homo-PE polymer having density 950 ± 5 kg/m^3. The copolymer density was higher and de-

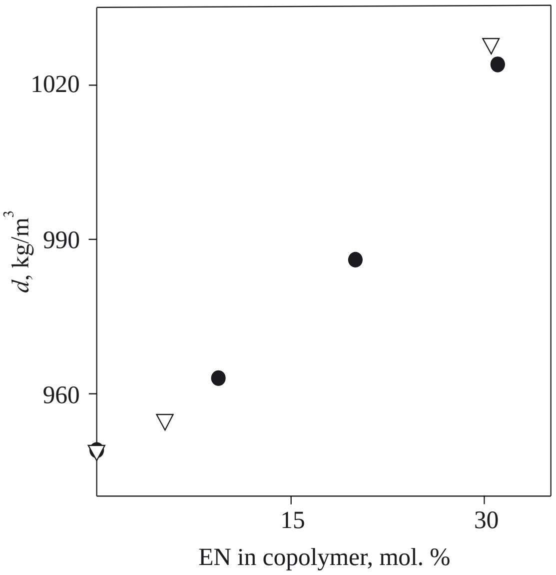


Fig. 1. Density (d) of ethylene/EN copolymers versus content of EN in copolymers obtained in the presence of Et[Ind]$_2$ZrCl$_2$/MAO (▽) or Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO (•) catalysts

pended on the EN content, namely grew with increasing content of EN units in the product.

Product structure

X-ray diffractograms in Fig. 2 represent the model compositions prepared by mechanical mixing of PE and poly-EN (PEN) homopolymers in different ratios, while those in Fig. 3 characterize ethylene/EN copolymers with different contents of EN. The set of diffractograms taken for the homopolymers mixtures (Fig. 2) simply reflects variations in the partial mass contents of the individual components in the compositions (PE/PEN). At the same time, in the diffractograms for a series of ethylene/EN copolymers (Fig. 3), the peaks belonging to crystalline PE phase can be seen only for the copolymers having ethylene mass content above 13 wt. % (Fig. 3, curves 3 and 4). Moreover, contrary to the homopolymer mixtures, changes in molecular compositions of copolymers were manifested in spectracular shifts of the amorphous halos toward to lower scattering angles. For instance, a partly crystalline copolymer having EN content equal 50 wt. % has shown the amorphous halo peak at 2θ = 18.9^o (curve 4), while an amorphous copolymer with EN content equal 87 wt. % has exhibited the maximum at 2θ = 17.4^o (curve 2). The diffractogram of PEN homopolymer (Fig. 3, curve 1) shows the amorphous halo with two maxima at 16.3^o and 22^o, which is similar to that observed for the unsubstituted norbornene homopolymer.

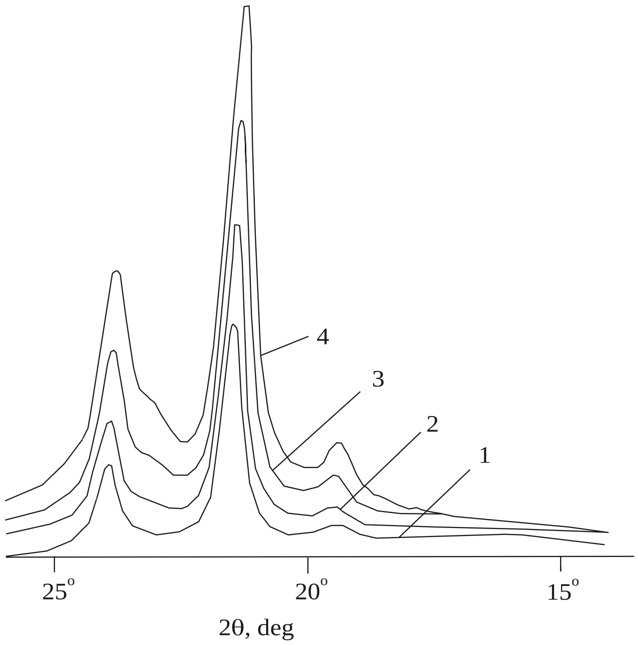


Fig. 2. Wide-angle X-ray diffraction patterns of PE/PEN mixtures (1—3) and PE (4) (intensity was normalized — 10^4 impulse/s); [PEN] in mixture, wt. %: 47 (1), 31 (2), 21 (3)

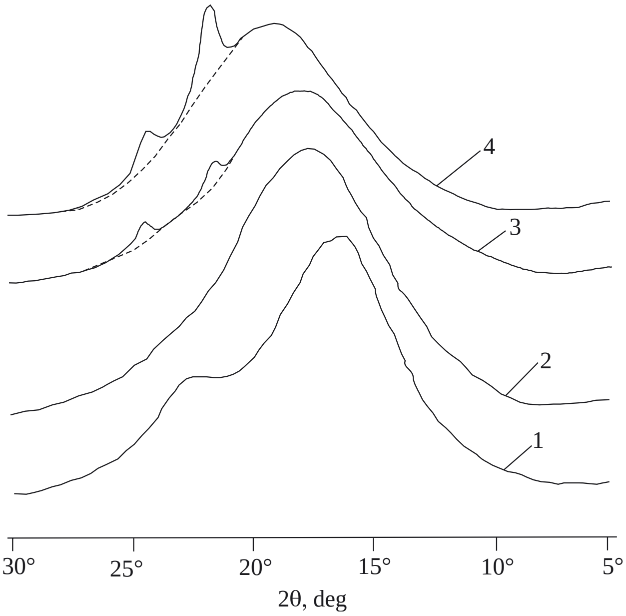


Fig. 3. Wide-angle X-ray diffraction patterns of PEN (1) and ethylene/EN copolymers (2—4) (intensity was normalized — 10^4 impulse/s); [EN] in copolymer, wt. %: 87 (2), 66 (3), 50 (4)

As it was stated before, to investigate a supramolecular structure of the prepared copolymers a method of very cold neutrons (VCN) scattering has been employed in this work. The essence of VCN

Table 4. Supramolecular structure and optical transparency of PE and ethylene/EN copolymers

No. (see Table 1)	[EN] in copolymer mol. %	X-ray studies		Very cold neutron scattering		Transparency$^{b)}$ (λ = 750 nm), %
		χ	$(L_{200} + L_{110})/2$, nm	φ	l, nm	
1	0 (PE)	0.77	12.0	n.d.$^{a)}$	n.d.	56.0
2	5.3	0.47	8.5	0.5	13.0	n.d.
4	30.5	amorphous	0	0.1	10.0	77.2
7	0 (PE)	0.64	24.0	n.d.	n.d.	36.0
8	62.0	amorphous	0	transparent	0	n.d.
11	9.4	0.31	8.0	0.3	12.0	n.d.
12	20.0	amorphous	0	0.2	8.7	73.5
13	31.0	amorphous	0	transparent	0	84.7

$^{a)}$ Not determined. $^{b)}$ The light transmission through support = 89.9 %.

method lies in the fact that for interactions of very cold neutrons with a substance, a total macroscopic cross sections are examined as a function of the neutron wavelength; dependences relating to elastic noncoherent VCN scattering from elements of supramolecular structure are discriminated and approximated by analytical expressions that enable one to determine the parameters of this structure (average size *l* and the volume fraction φ and shape) [14—16].

The data obtained as the results of probing of the supramolecular structure of ethylene/EN copolymers using X-ray diffraction and VCN scattering methods are summarized in Table 4. It can be seen that when the content of EN units in the partly crystalline ethylene/EN copolymers grows, the overall degree of crystallinity (crystal phase content, χ) as well as the crystallites dimensions tend to decrease and, eventually, the copolymer becomes completely amorphous.

It is worth noting that the X-ray diffraction and VCN scattering methods employed by us for probing of the supramolecular structure of the prepared copolymers may give to some extent controversial results. Specifically, the mean dimensions of the supramolecular formations, evaluated with the aid of VCN scattering, for several copolymers appeared to be higher than those found by X-ray diffraction (Table 4, samples 2 and 11). Furthermore, according to the X-ray data, the samples 4 and 12 are devoid of any crystalline phase, while VCN scattering data for the same samples indicated the presence of inhomogeneities having the mean diameters values of 10.0 and 8.7 nm, the volume fractions of them being equal to 0.1 and 0.2, respectively. Probably, the observed discrepancies are related to the fact that X-ray diffraction is mainly sensitive to strictly ordered crystalline domains while VCN scattering is capable to detect some almost amorphous or highly defective structures as well.

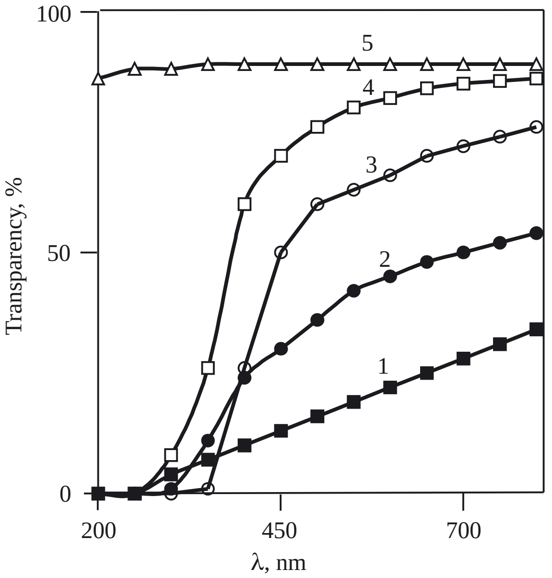


Fig. 4. Light transmission through PE (1), ethylene/EN copolymers (2—4) and support (5) versus wavelength (λ); [EN] in copolymers, mol. %: 5.3 (2), 20 (3) or 50 (4)

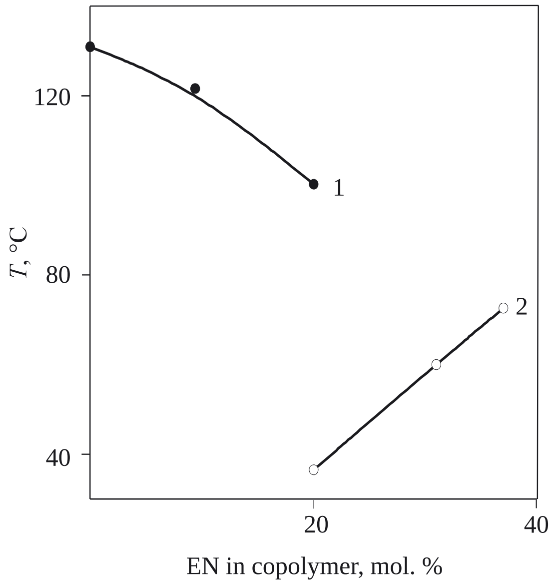


Fig. 5. T_m (1) and T_g (2) of ethylene/EN copolymers obtained in the presence of $Me_2Si[Ind]_2ZrCl_2/MAO$ catalyst versus content of EN

Notably, the possibility of presence of the latter structures in the studied ethylene/EN copolymers has been supported also by the observed lower optical transparency of the samples 4 and 12 (Table 4) as compared, *e.g.*, to the sample 13, the latter being categorized as perfectly amorphous material in terms of both the X-ray and VCN scattering analyses data.

General optical characteristics of the prepared copolymers in the near UV and visible parts of light spectrum have been studied. The data relevant to optical properties of both PE and ethylene/EN copolymers are presented in Table 4 and in Fig. 4. The transmittance of the copolymers has been growing with increasing EN units' content in the copolymer main chain. For the copolymers samples containing up to 20 mol. % of EN units, gradual formation of zones of transparency in UV and visible parts of light spectrum has been noted, while at higher contents of EN in the copolymer main chain the materials showed rather fair general transparency (T > 50 % at λ > 350 nm).

Thermal properties

The prepared copolymers have exhibited thermal properties clearly dependent on their compositions. Some thermal properties of ethylene/EN copolymers in comparison with those of homo-PE and homo-PEN samples have been studied by DSC and are summarized in Fig. 5 and Table 5. DSC data of PP and propylene/EN copolymers are presented in Table 6. Table 6 contains also the results of investigations concerning PP + copolymer compositions (sample 17). This composition shows some crystallinity contrary to completely amorphous sample of copolymer 16.

T a b l e 5. Results of DSC investigations of PE and ethylene/EN copolymers[a)]

No. (see Table 1)	[EN] in copolymer mol. %	ΔH J/g	Crystallinity[b)]	T_m, °C	T_g, °C
1	0 (PE)	174.42	0.59	133.2	below 0 °C
2	5.3	92.56	0.33	124.7	below 0 °C
3	28.0	—	amorphous	—	81.2
4	30.0	—	amorphous	—	85.0
6	100.0 (PEN)	—	amorphous	—	57.6
7	0 (PE)	—	0.66	136.4	below 0 °C
8	62.0	—	amorphous	—	69.0
9	100.0 (PEN)	—	amorphous	—	65.2
10	0 (PE)	175.85	0.60	131.0	below 0 °C
11	9.4	78.76	0.27	121.6	below 0 °C
12	20.0	11.30	0.03	100.2	36.5
13	31.0	—	amorphous	—	60.0
14	37.0	—	amorphous	—	72.6

a) Second melting.
b) Calculated in view of ΔH of PE monocrystal equal to 294 J/g.

According to the DSC data and in good correlation with the mentioned above X-ray and VCN scattering data, the partly crystalline ethylene/EN copolymers have shown spectacular loss of their crystallinity degree with increase in the partial EN units content in the copolymer. In this way, the crystal phase melting enthalpy values have progressively decreased and the endotherm peak has gradually shifted to lower temperatures. Further increase in EN content has led to disappearance of the endotherm at DSC curves, thus indicating the approach to a critical composition of the copolymer beyond which the materials of this type would exist in perfectly amorphous state. As it is well known, the glass transition (T_g) of PE homopolymers is at temperatures below 0 °C. Incorporation of 5-ethylidene-2-norbornene units into the polyethylene main chain leads to a considerable increase in T_g value of the resulting material. Among the copolymers studied in this work, the highest T_g value of 85 °C has been observed for a copolymer containing 30 mol. % of 5-ethylidene-2-norbornene and prepared in the presence of Et[Ind]$_2$ZrCl$_2$/MAO catalyst system.

T a b l e 6. Results of DSC investigations of PP, propylene/EN copolymer and the composition of PP + propylene/EN copolymer

No. (see Table 1)	Polymer product			DSC results[a)]			
	Compositions	[EN], mol. %	[C=C], mol/g	ΔH, J/g	Crystallinity[b)]	T_m, °C	T_g, °C
15	PP[c)]	—	$0.16 \cdot 10^{-3}$	81.4	50	127	below 0 °C
16	Propylene/EN	50.0	$5.70 \cdot 10^{-3}$	1.4	amorphous	—	55
17[d)]	PP + propylene/EN	9.7	$0.80 \cdot 10^{-3}$	64.3	39	124	below 0 °C

a) Second melting. b) Calculated in view of ΔH of PP monocrystal equal to 165 J/g. c) M_n = 6250. d) Content of copolymer in the composition 17 = 35 wt. %; [EN] in propylene/EN copolymer = 65 mol. %.

Ozonolysis of ethylene/EN copolymers

The ethylene/EN copolymers showing good thermal and optical properties can further benefit from the availability of side double bonds in their chains, which are able to participate in the ozonolysis reaction, as has been mentioned above. The highest content of the ethylidene >C=CH-CH$_3$ groups in the copolymers prepared by us was $6.9 \cdot 10^{-3}$ mole/g (Table 2). For comparison, the content of the same groups in a homopolymer of 5-ethylidene-2-norbornene was found to be $8.3 \cdot 10^{-3}$ mole/g, while the content of terminal C=C groups in a homo-PE having, *e.g.*, M_n = 100.000, is only close to $5 \cdot 10^{-5}$ mole/g. Therefore ozonization of ethylene/EN copolymers is a convenient way of modification of PE-based polymers by generation of the polar pendant groups at the main chain. The rate constants of ozone interaction with double bonds [10^5 l/(mol · s)] by several orders of value exceed those characteristic for reactions of O$_3$ with the other groups [10]. Ozonides of organic compounds, like many other derivatives from the peroxides' class, readily decompose during storage or under heating and the main decomposition products are corresponding aldehydes and carbonic acids [25].

According to our FTIR data, ozonolysis of the >C=CH-CH$_3$ pendant groups at the main chain of the copolymers under study seems to lead to generation of a lot of derivative functional groups. A series of absorption bands in the vicinity of 1700—1725, 1740 and 1750 cm^{-1}, obviously, originate from the vibrations of a carbonyl moiety in aliphatic carboxylic acids, ketones and aldehydes, respectively. The IR spectra of the ozonizated copolymers, obtained in this work, normally show rather strong absorption at 1825 cm^{-1} which can be assigned either to aliphatic anhydride (-OC-O-CO-) or to peroxides of saturated carboxylic acids (-CO-O-O-CO-) [26].

One more absorption characteristic for the ozonizated material appears in the range of 1150—1040 cm^{-1} and, most probably, belongs to the stretch vibration of

>C-O- group. Therefore one can not exclude the possibility of aliphatic ethers formation in the result of ozonolysis of such copolymers, as the asymmetric stretching of aliphatic ethers bonds (>C-O-C<) is normally observed at the same frequency range (1140—1085 cm^{-1}).

CONCLUSIONS

The results of the present study have confirmed the feasibility of functionalization of the main chain of PE (PP) with pendant ethylidene groups by means of copolymerization of ethylene with a cyclic EN comonomer. It is shown that ethylidene function of the cyclic EN does not play role in the copolymerization reaction, thus provides the resultant copolymer chain with the reactive sites amenable to further functionalization or polymer-analog transformations.

For the first time, the molecular compositions of ethylene/EN copolymers have been determined in this work by employing the ozonolysis of ethylidene double bonds belonging to the cyclic EN comonomer units incorporated into the copolymer backbone.

Also for the first time, to clarify peculiarities of supramolecular structure of ethylene/EN copolymers under study, the corresponding X-ray diffraction results have been compared in this work with those obtained by VCN scattering method.

It is established that the copolymers of ethylene and 5-ethylidene-2-norbornene (as well as those of ethylene and unsubstituted norbornene [27]) are able to show high density (d) and high glass transition temperature (T_g) together with high optical transparency. It was found that the structure of the metallocene catalyst employed and the partial content of the cyclic comonomer in the copolymer are the main factors determining the properties of the polymer materials prepared and studied in this work.

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