

Functionalized polymers from Ziegler–Natta catalysts¹

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Abstract

A new method for the preparation of functionalized polyolefins is presented. The method consists of two steps: (i) copolymerization of ethylene and/or an α -olefin with 1-iodo-3-butene (ii) elimination or substitution reaction of the iodine atom, by reaction with an organic salt of potassium, in the presence of a crown ether.

The synthesis of ethylene/propylene/1-iodo-3-butene copolymers with Vanadium based catalysts as well as the dehydrohalogenation reaction on the copolymers are discussed.

The first example of ethylene/propylene/1,3-butadiene copolymers, where the diene has exclusively 1,2 configuration, is presented.

Keywords: 1,3-Butadiene copolymers; 1-Chloro-3-butene; ¹³C-NMR analysis; Dehydrohalogenation reaction; Ethylene copolymers; ¹H-NMR analysis; 1-Iodo-3-butene; Olefins; Propylene copolymers; Vanadium

1. Introduction

It is known that the introduction of functional groups in the olefinic polymers is a useful method for improving their chemical and physical properties, such as compatibility to polar polymers, dyeability, adhesiveness to metals, gas impermeability etc.

As reported in the literature, functionalized polyolefins can be prepared by: (i) chemical modification reactions or free radical graft polymerization on preformed polyolefins and (ii) copolymerization of α -olefins with polar monomers [1,2].

As far as the latter method is concerned, it is also known how difficult it is to prepare olefin copolymers containing nitrogen or oxygen atoms, by using Ziegler–Natta catalysts [2,3]. The interaction of the Lewis acid components of the catalytic system with the heteroatoms of the polar monomers brings about the poisoning and the deactivation of the catalytic sites.

One of us first reported the preparation of functionalized polyalkenes with Ziegler–Natta catalysts, by polymerizing oxygen or nitrogen containing monomers [4]. In this work the basic criteria for increasing the polymerizability of polar monomers at Ziegler–Natta sites were exploited: to insert methylene units as spacers between the double bond and the heteroatom, to

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¹ This paper is dedicated to the memory of Dr. Umberto Zucchini.

increase the steric hindrance and to lower the electron-donating nature of the heteroatom.

Clark reported the pretreatment of the polar monomers with an organometallic Al compound as a method to reduce their reciprocal reactivity [5].

Another way proposed was the use of monomers containing ester groups [6], less reactive towards Ziegler–Natta catalysts. However, although long chain ω -ester-1-olefins were used, the content of ester groups in the copolymer was less than 5% by moles. Higher levels could be reached only by using particularly hindered esters [7].

More recently, α - ω dienes, previously reacted with boranes, were used by Chung as monomers [8–11].

In the present paper, a new versatile method for preparing functionalized polyolefin through a Ziegler–Natta process [12] is presented.

The method consists of two steps:

- (i) copolymerization of ethylene and/or an α -olefin with 1-iodo-3-butene
- (ii) elimination or substitution reaction of the iodine atom, by reaction with an organic salt of potassium, in the presence of a crown ether.

By this procedure, it is possible to prepare functionalized polyolefins, ranging from elastomeric copolymers of ethylene and propylene to isotactic polypropylene, containing a large variety of functional groups, for example: CH=CH₂, OR, OH, OCOR, (COOR)₂, NR₂.

The preparation of elastomeric copolymers of ethylene and propylene with 1-iodo-3-butene and the dehydrohalogenation reaction are hereinafter discussed. The first example of ethylene/propylene/1,3-butadiene copolymers, where the diene has exclusively 1,2 configuration, is presented.

The results obtained in the preparation of elastomeric copolymers of ethylene and propylene as well as of isotactic polypropylene containing polar groups will be discussed in a forthcoming paper [13].

2. Experimental

All the operations involving air sensitive compounds were carried out by using the known Schlenk-tube technique.

Solvents were purified according to known methods [14].

2.1. Catalysts

V(acac)₃ (Fluka, >95%) was further purified through crystallization from a toluene solution.

Al(C₂H₅)₂Cl and Al(C₂H₅)₂I (Schering) were used without further purification.

2.2. Synthesis of ω -halo- α -olefins

3-Buten-1-ol (Fluka, >98%), SOCl₂ (Carlo Erba, >99%), toluene-4-sulfonyl chloride (Fluka, >99%), NaI (Carlo Erba, >99.5%) were used without further purification.

Synthesis of 1-chloro-3-butene. The reaction between 3-buten-1-ol and thionyl chloride was carried out according to the reported procedure [15–17]. The product was purified through rectification (b.p. 73.2–73.9). ¹H-NMR (200 MHz, C₆D₆): δ 5.80 (m, 1H, =CH), 5.02 (m, 2H, =CH₂), 3.33 (t, 2H, –CH₂I–), 2.24 (q, 2H, –CH₂–).

Synthesis of 3-butene-1-*p*-tolyl sulfonate. The reaction between 3-buten-1-ol and *p*-toluene-sulfonyl chloride was carried out according to a standard procedure [18]: In a 3 neck round bottomed flask, equipped with thermometer and mechanical stirrer, 25 ml of 3-buten-1-ol and 100 ml of pyridine were introduced. By using a ice bath, the temperature was taken to 4°C. *p*-Toluene-sulfonyl chloride was added in portions and the temperature was kept below 11°C. The mixture was stirred at 15°C for 3 h. It was then poured into a mixture of 400 ml of ice and 100 ml of HCl. The organic layer was extracted with CH₂Cl₂ and the product isolated by evaporation of the chlorinated solvent. Average yield: 97%. ¹H-NMR (300 MHz, CDCl₃): δ 7.78 (d, 2H, *o* Ph), 7.35 (d, 2H, *m* Ph), 5.65 (m, 1H, –CH=), 5.05 (m, 2H, =CH₂),

4.05 (t, 2H, $-\text{OCH}_2-$), 2.45 (s, 3H, $-\text{CH}_3$), 2.40 (q, 2H, $-\text{CH}_2-$).

Synthesis of 1-iodo-3-butene. The reaction with NaI was performed as described in the literature, starting from either 3-buten-1-ol [19,20] or from 3-butene-1-*p*-tolyl sulfonate [21]. The reaction yields were 65% and 75% respectively. $^1\text{H-NMR}$ (200 MHz, C_6D_6): δ 5.40 (m, 1H, $=\text{CH}$), 4.91 (m, 2H, $=\text{CH}_2$), 2.61 (t, 2H, $-\text{CH}_2\text{I}-$), 2.14 (q, 2H, $-\text{CH}_2-$).

2.3. Reaction between 1-iodo-3-butene and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{V}(\text{acac})_3$

In a 10 ml Schlenk vial, 1 ml of deuterated benzene (C_6D_6), 44 mg (0.24 mmol) of 1-iodo-3-butene and 24 mg (0.20 mmol) of AlEt_2Cl were introduced. The solution was stirred at 40°C for 2 h and then at room temperature for 16 h. A sample was taken for $^1\text{H-NMR}$ analysis (see Fig. 1b). 2.3 mg of $\text{V}(\text{acac})_3$ (0.0067 mmol) were then added and the mixture was stirred at 40°C for 3 h. A sample of the supernatant solution was analyzed by $^1\text{H-NMR}$ (see Fig. 1c).

2.4. Polymerizations

Polymerizations were performed either in a 100 ml or in a 1 l (Büchi) glass autoclaves. The former was equipped with a magnetic stirrer, a thermocouple and valves for the introduction of catalyst, liquids and gases. The Büchi autoclave was equipped with a mechanical stirrer, a thermocouple, a jacket, a high pressure syringe for the introduction of the catalyst solution, and valves for the introduction of liquids and gases.

Ethylene/propylene and ethylene/propylene/1-iodo-3-butene copolymerizations were performed by supplying the ethylene/propylene mixture at a constant flow rate (0.5 l/min). The ethylene/propylene ratio was kept constant by an automatic gas blending device.

The following standard procedure was employed: a solution of the alkyl aluminum in toluene was introduced into the autoclave. The solution was then saturated with the ethylene/

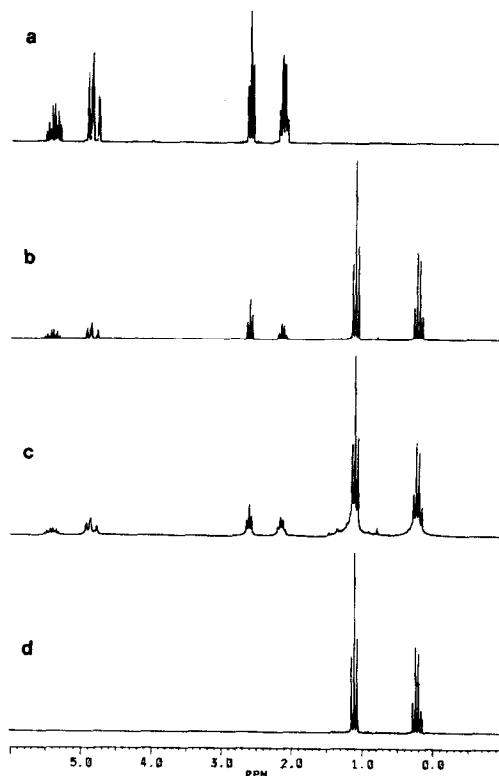


Fig. 1. Reaction between 1-iodo-3-butene and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{V}(\text{acac})_3$. $^1\text{H-NMR}$ of the halo-olefin (1a), the chlorinated alkyl aluminum (1d), the reaction products after 2 h at 40°C and 16 h at RT (1b) and the reaction products after the addition of $\text{V}(\text{acac})_3$ and 3 h at 40°C .

propylene mixture and thermostated at the polymerization temperature. In the case of copolymerizations with 1-iodo-3-butene, the halo-olefin was added at this point. A solution of $\text{V}(\text{acac})_3$ in toluene was then introduced and the pressure brought to the level fixed for the polymerization. When the polymerization was carried out in the Büchi autoclave, the pressure was increased before the addition of the catalyst, which was then injected by using the aforementioned syringe. Polymerizations were stopped by injecting few ml of methanol. The polymers reported in the present paper were recovered by twice washing the polymer solution with $\text{H}_2\text{O} + \text{HCl}$, H_2O , $\text{Na}_2\text{S}_2\text{O}_3$, H_2O and by precipitating them with methanol. The conversion of the reaction was calculated according to the following expression: $\text{Conversion} = 100 \cdot (I_i - I_e) / I_i$, where I_i and I_e are the iodine contents before and after the reaction.

2.5. Dehydrohalogenation reaction

Potassium *tert*-butylate (Fluka, >97%) and 18-crown-6 (Fluka, >98%) were used without further purification.

A standard procedure was followed for all the reactions. Entry 12 of Table 4 is reported as an example. In a 10 l autoclave, equipped with mechanical stirrer, thermocouple, condenser, dropping funnel and valves for the introduction of liquids and gases, 7.5 l of toluene were introduced. The autoclave was thermostated at 90°C. 11.1 g of the terpolymer were dissolved and 10.4 ml of a 0.135 M solution of 18-crown-6 in toluene were introduced. 4.8 g of $t\text{BuO}^- \text{K}^+$ were then added. After 18 h, 10.4 ml of the crown ether solution and 4.8 grams of $t\text{BuO}^- \text{K}^+$ were added. The reaction was stopped after 6 more hours, by adding few ml of methanol. The polymer was recovered by evaporation of about half of toluene and precipitation with methanol.

2.6. Polymer characterization

The content of iodine in the polymers was determined through potentiometric titration by means of a Potentiograph E 3367 Metrohm Herisau. First a standard solution of NaI (161 mg in 100 ml) was prepared and titrated three times with a 0.01 M solution of AgNO_3 . The average consumption of AgNO_3 was then calculated. About 30 mg of polymer were burned and dissolved in a water solution containing $\text{Na}_2\text{S}_2\text{O}_2$, and 2 ml of standard solution of NaI were added. Titration with NaI was carried on and the difference of consumption of AgNO_3 with respect to the analysis on the pure standard was converted into wt% of iodine in the polymer. The minimum level of iodine detection was estimated to be about 0.3%.

^1H and ^{13}C -NMR spectra of the terpolymers were run at 383 K on a Bruker AM300 spectrometer, operating at 300.13 MHz with a 5 mm probe for ^1H -NMR and at 75.43 MHz with a 10 mm probe for ^{13}C -NMR spectra. Samples were dissolved in $\text{C}_2\text{D}_2\text{Cl}_4$ with the following concentrations: 3% w/v for ^1H -NMR and 10% w/v for

^{13}C -NMR. Chemical shifts were referred to TMS = 0.0 ppm.

IR spectra were recorded on a Perkin Elmer 1760 instrument.

Thermal analysis were performed with a Perkin Elmer DSC-7, in a range from -130°C to 120°C at a heating rate of $20^\circ\text{C}/\text{min}$.

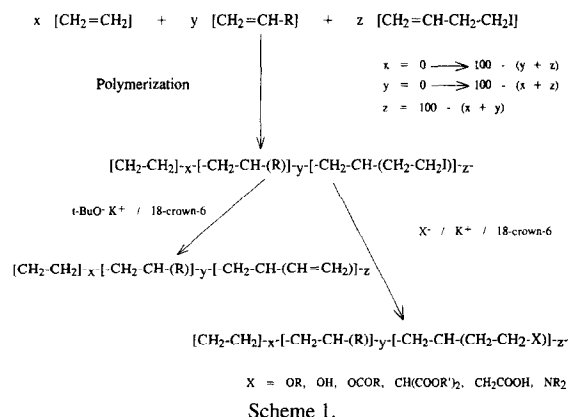
Intrinsic viscosity measurements were carried out with a Hubbel–Hode type viscometer by using 0.10 wt% solutions in 1,2-dichlorobenzene at 135°C , with no kinetic-energy corrections.

Gel permeation chromatography (GPC) analysis were carried out by using a Waters ALC/GPC 150-C chromatograph, equipped with a refractive index detector and with 4 linear PLGEL columns, working at 135°C with 1,2-dichlorobenzene as solvent. Average molecular mass calculations were performed by using universal calibration, proposed by Benoit et al. [22]. Monodisperse polystyrenes were used as standards. The fit for linear polyethylene and polypropylene, corrected for average composition according to Scholte et al. [23] was used.

Fractionation of the copolymers was carried out by direct extraction, by using, in sequence, solvents (pure or in mixture) with increasing solubility power. Working temperature was the boiling point of the solvent or of the mixture. The procedure was as follows. In a round-bottomed flask, equipped with a mechanical stirrer, 600 ml of solvent(s) and 6.0 g of copolymers were introduced. The mixture was allowed to reflux for 6 h under a dry nitrogen atmosphere. The fractions were recovered either by evaporating the solvents under reduced pressure or by precipitation with a poor solvent, and were dried under vacuum at 60°C .

3. Results and discussion

The method, presented in this paper, for the preparation of functionalized polyolefins, is summarized in Scheme 1.



3.1. Halogenated monomer: 1-iodo-3-butene

The polymerizability of halogenated olefins with Ziegler–Natta catalysts is much reduced by their reactivity with the organometallic components of the catalytic system. Clark and Powell reported on the polymerization of ω -halo-1-olefins [24], with TiCl_3 as catalyst and AlEt_2Cl as cocatalyst. They concluded that the influence of deactivation reactions could be decreased by increasing the size and the distance from the double bond of the halogen atom and by using primary alkenyl halide.

In a patent registered to Hoechst [25], crystalline copolymers of propylene with linear ω -halo-1-olefins were obtained, with reasonable polymerization activity, by using TiCl_3 and AlEt_3 as catalysts.

Table 1

Synthesis of ethylene/propylene/1-iodo-3-butene (Ib) copolymers with $\text{V}(\text{acac})_3$ as catalyst and $\text{Al}(\text{C}_2\text{H}_5)_2\text{X}$ [X = Cl, I] as cocatalyst

Entry	$\text{V}(\text{acac})_3$ (mg)	AlEt_2X	Al/V (mol/mol)	C_3/C_2 (mol/mol)	Ib (ml)	Toluene (ml)	T ($^\circ\text{C}$)	time (min)	Activity (g polymer/g V)
		X = mmol/l							
1	25.3	I 57.5	32	2	0	40	35	45	670
2	25.3	I 57.5	32	2	0.4	40	35	45	330
3	235	I 60	35.6	2	5.5	400	35	150	350
4	540	I 57.5	29.7	2	12.5	800	45	120	255
5	570	I 57.5	28.2	2	12.5	800	45	120	250
6	540	I 57.5	29.7	2	13	800	45	120	235
7	520	I 57.5	30.9	2	16	800	45	120	215
8	82	Cl 8	33	2.5	8	500	40	240	300
9	280	Cl 24	30	3.5	8	400	40	240	120
10	280	Cl 24	30	5	8	400	40	240	100

Polymerization conditions: total pressure = 4 atm.

The choice of 1-iodo-3-butene as the halo-olefin for the preparation of functionalized polyolefins, according to Scheme SCHEME, was thus based on two main considerations:

- (i) the literature results, indicating linear iodo-olefins as suitable for Ziegler–Natta polymerization
- (ii) the possibility of obtaining new interesting products, through elimination or substitution reaction of iodine.

1-Iodo-3-butene was prepared starting from 3-buten-1-ol and following two synthetic pathways, according to the methods reported in the literature:

- (i) synthesis of 1-chloro-3-butene, by reaction with SOCl_2 [15–17] and subsequent treatment with NaI [19,20]
- (ii) synthesis of 3-butene-1-*p*-tolyl sulfonate [18] and then reaction with NaI [21].

The latter method, without any particular optimization of the reaction conditions, gave a global yield of about 75%.

3.2. Ethylene and propylene copolymerization with 1-iodo-3-butene

Polymerization conditions and copolymer characteristics are reported in Table 1 and Table 2, respectively.

Copolymerizations were performed by using vanadium tris-acetylacetonate [$\text{V}(\text{acac})_3$] as catalyst.

Table 2

Characterization of ethylene/propylene/1-iodo-3-butene copolymers obtained with $V(acac)_3$ as catalyst and $Al(C_2H_5)_2X$ ($X = Cl, I$) as cocatalyst

Copolymer	C_3 (wt%)	Iodine (wt %)	$[\eta]$ (dl/g)
1 ^a	35.2	0	5.00
2 ^a	36.4	3.6	2.81
3	38	2.8	3.00
4	35.4	4.3	2.50
5	37.5	4.1	2.62
6	35	3.7	2.60
7	37.8	4.8	2.55
8	19	1.6	0.68
9	27	2.1	1.00
10	40	2.1	0.66

^a GPC analysis. $M_w \cdot 10^{-3}$ (g/mol) = 560 (peak 1), 4 (peak 2) for copolymer 1; 680 (peak 1), 2 (peak 2) for copolymer 2.

Best results were obtained with $Al(C_2H_5)_2I$ [$AlEt_2I$] as cocatalyst. As it will be shown hereinafter, good consistency was obtained as far as polymerization results and copolymer characteristics are concerned.

The polymerization activity was affected by the presence of 1-iodo-3-butene in the polymerization mixture. From the comparison of Entry 1 and Entry 2, it appears that, with respect to a copolymerization carried out in the absence of the halo-olefin, the activity was reduced to about one half, when the concentration of 1-iodo-3-butene in the polymerization mixture was about 2% by weight. Furthermore, by comparing Entries 2–7 a gradual decrease of the polymerization activity may be observed, as the concentration of 1-iodo-3-butene increases.

The halo-olefin had no influence on the chemical composition of the copolymers, as indicated by the propylene content of copolymers 1–7.

By contrast, a strong effect was observed on the molecular mass, as it appears from the comparison of the viscosities of the iodine containing copolymers and of copolymer 1.

By using $Al[(C_2H_5)_2]Cl$ as cocatalyst, copolymers were obtained with lower molecular mass and lower propylene and iodine content, with respect to the copolymers obtained with $AlEt_2I$ as alkyl aluminum. The lower iodine content can not be attributed to the interaction of the different components of the catalytic system with the iodo-olefin. This interaction was investigated by 1H -NMR spectroscopy (see Fig. 1). By mixing $AlEt_2Cl$ and 1-iodo-3-butene, in benzene, under experimental conditions similar to those adopted in polymerization, but in a much more concentrated solution, no reaction was observed, even after several hours. Also after the addition of $V(acac)_3$, it was not possible to detect in the NMR spectrum signals due to compounds other than the iodo-olefin and the chlorinated alkyl aluminum.

All the copolymers reported in Table 2, having at least 35% by weight as propylene content, were essentially amorphous.

Copolymers obtained with $V(acac)_3$ and $AlEt_2I$ as catalytic system, with or without 1-iodo-3-butene as comonomer, showed a bimodal distribution of the molecular masses. To investigate whether this phenomenon was related to a chemical inhomogeneity of the copolymers, the chem-

Table 3

Fractionation of an ethylene/propylene/1-iodo-3-butene copolymer (copolymer 3)

Fraction	Solvent	Amount wt%	C_3 wt%	Iodine wt%	$M_w \cdot 10^{-3}$		peak 1/peak 2 wt/wt
					peak 1	peak 2	
Raw sample	–	100	38	2.8	n.d.	n.d.	n.d.
1	ether/acetone = 50/50	2.6	33.4	n.d.	–	1.4	–
2	ether/acetone = 90/10	13.5	39	3.4	265	3.3	0.2
3	ether	10.7	50.9	2.4	411	5.1	5
4	ether/hexane = 80/20	60.9	36.8	2.2	330	5.1	12
5	hexane	7.6	27.8	1.8	512	6.3	3
6	heptane	0.9	24.3	1.8	712	7	4
7	residual	3.7	14.6	2.3	712	–	–

ical composition distribution of copolymer **1** was evaluated through fractionation, by using a proper solubility driven method (see Table 3). It is well known the influence on a copolymer fractionation of the interaction parameters of the solvent with the comonomer units [26,27]. The greater is the difference among these parameters and the higher is the efficiency of the fractionation. To maximize this difference, we have developed a separation method that employs a sequence of solvents of different polarity, pure or in mixture (see Experimental). A bimodal distribution was detected in fractions 2–6, that represents almost the totality of the copolymer. The distribution of the propylene content appears to be not highly homogeneous. However, for more than 80% of the copolymer (Fractions 2–4) this content was in a rather narrow range. Fraction 4 has a propylene content higher than Fraction 3. This apparent inversion in the order of fractionation is due to the high molecular mass of the fraction. The iodo-olefin was homogeneously distributed, at least in the high molecular mass fractions, that are the largest part of the copolymer (more than 80% by weight). More particularly, the amount of iodine of fraction 7, which was monomodal, was very similar to the average value of the raw copolymer. Furthermore, the relative amount of the two peaks of the bimodal distribution was different in the various fractions. All these findings seem to suggest that the bimodal distribution was essentially due to the molecular masses, rather than to an inhomogeneous distribution of the chemical composition.

3.3. Preparation of ethylene/propylene/1,3-butadiene copolymers: dehydrohalogenation reaction

Dehydrohalogenations are well known reactions of organic chemistry [28]. Among all the methods available in the literature, we selected that reported by Dehmlow and Lissel [29].

They employed tBuOK in the presence of 18-crown-6 for the dehydrohalogenation of chloro- and bromo-alkanes. Depending on the alkyl-halogenide, the yield ranged from about

70% to about 95%. In most cases, at least 10% of alkyl-tert-butyl ether was present as side product of the reaction.

Substitution reaction of a halogen atom from a polymer, by using a sodium alkolate in the presence of a crown ether, was reported in the literature for poly(vinyl chloride) [30]. The maximum conversion reached was about 5% and polymer degradation occurred during the reaction.

Dehydrohalogenation reactions performed according to the aforementioned method, on ethylene/propylene/1-iodo-3-butene copolymers are reported in Table 4.

Optimization of the reaction conditions was performed, in order to reach a high efficiency for the dehydrohalogenation reaction, applied on a polymer, and to minimize the occurrence of the substitution reaction, which would lead to the formation of an ether group.

When tBuOK and 18-crown-6 were used according to the reported recipes [29], and therefore tBuOK was almost in stoichiometric ratio with respect to the iodine atom ($\text{tBuO}^-:\text{I}=1.22:1$), and the crown ether was present in a catalytic amount, poor results were obtained. When the reaction was carried out in n-heptane (see Entry 11), even under reflux and for a prolonged time, the iodine content of the polymer remained unchanged. By decreasing to about one half the tBuOK/18-crown-6 molar ratio and by using toluene as solvent (see Entry 12), about 15% of iodine was removed from the polymer and vinylic double bonds were detected in the IR spectrum. A reaction conversion of about 70% was reached in Entry 13, by using a large excess of alkolate (tBuOK/I=5:1) and by decreasing to less than one third, with respect to the literature values, the alkolate/crown ether ratio. A further increase of the crown ether amount (tBuOK/18-crown-6=5) led to a further improvement of the conversion (about 80% in Entry 14). However, the presence of ether groups was clearly detected in the IR spectrum, even if not quantitatively determined. A conversion higher than 90% was finally obtained by using the following molar ratios: tBuOK:I=10:1 and tBuOK:18-crown-

Table 4
Reaction of ethylene/propylene/3-iodo-1-butene copolymers with $t\text{BuO}^- \text{K}^+ / 18\text{-crown-6}$

Entry	Polymer		Solvent (type)	g polymer/l solv.	tBuOK/I (molar ratio)	tBuOK/18-crown-6 (molar ratio)	time (h)	Conversion (%) ^a
	g	I wt%						
11	0.27	4.2	heptane	0.9	1.1	110	48	0
12	0.42	4.2	toluene	1.4	1.3	47	5.5	13.7
13	0.78	5.2	toluene	3.9	5	30	24	70.6
14	0.70	5.2	toluene	7	5	5	24	80.6
15	0.48	5	toluene	3.9	10.1	39.9	24	>92
16	6.20	3.4	toluene	1.6	10.4	29.9	16	>91
					10.4	29.9	8	
17	11.10	4.9	toluene	1.8	10	30.2	16.5	>93.8
					10	30.2	7.5	
18	18.50	3.7	toluene	2.5	8	30	18	>92
					8	30	6	
19	19.60	4.1	toluene	2.6	8	30	18	>92.6
					8	30	6	
20	10.50	9.2	toluene	3	10	30	18	>96.7
					10	30	6	

^a The conversion is calculated as reported in the Experimental part. As the minimum content of iodine detectable was 0.3 wt%, the values reported, from Entry 15 on, indicate that the iodine detected was < 0.3 wt%.

Table 5
Characterization of ethylene/propylene/1,3-butadiene copolymers

Copolymer	[η]		Butadiene wt%
	before reaction	after reaction	
11	n.d.	n.d.	0.15
12	n.d.	n.d.	0.3
13	3	2.8	0.9
14	2.1	2	1.6
15	n.d.	n.d.	1
16	3	2.62	1.5
17	2.65	2.6	1.2
18	2.6	2.53	1.6
19	2.62	2.55	1.3
20	n.d.	2.7	3.6

6 = 30:1. To ensure almost complete removal of iodine, a double addition of the reagents was performed (see Entries 16–19). The iodine left in the polymer was below the threshold of the experimental sensitivity of the analytical method employed.

The characterization of ethylene/propylene/1,3-butadiene copolymers obtained from the dehydrohalogenation reaction is collected in Table 5. The copolymer composition was investigated ¹H-NMR analysis. In Fig. 2 (a) the spectrum of copolymer 14 is reported. The triplet at

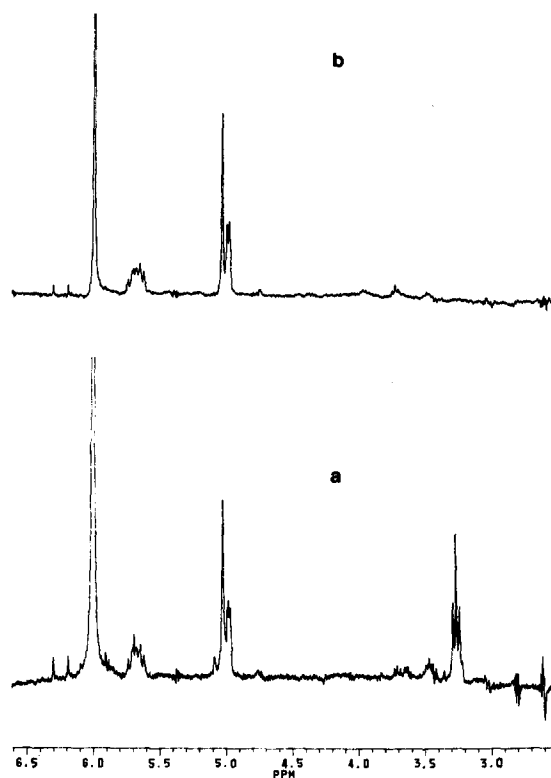


Fig. 2. 2(a): ¹H-NMR spectrum of a sample of ethylene/propylene/1-iodo-3-butene dehydrohalogenated (copolymer 14 of Table 5). 2(b) ¹H-NMR spectrum of an ethylene/propylene/1,3-butadiene copolymer (copolymer 15 of Table 5).

3.27 ppm, arising from $-\text{CH}_2-\text{CH}_2-\text{I}$ group, clearly indicates the incomplete conversion of the dehydrohalogenation reaction. Besides the peaks between 0.5 and 2 ppm, arising from aliphatic protons and not reported in the Figure, two multiplets due to the vinylic group $\text{C}^1\text{HaHb}=\text{C}^2\text{Hc}$ are present: $\text{Ha} = 5.0$ ppm, $J_{\text{Ha,Hb}} = 11.8$ Hz; $\text{Hb} = 4.99$ ppm, $J_{\text{Hb,Hc}} = 16.8$ Hz; $\text{Hc} = 5.67$ ppm. In Fig. 2 (b) the $^1\text{H-NMR}$ spectrum of copolymer **15** is reported. In this case, peaks due to iodo-butene are not detectable. On the basis of the NMR results, it can be stated that a high selectivity was obtained in the elimination with respect to the substitution reaction of iodine. As a matter of fact, signals due the ether group are hardly detectable in the reported spectra. When the dehydrohalogenation reaction was performed on a copolymer with higher iodine content, as in Entry 20, it was possible to determine that the amount of the ether group was less than 10% with respect to the vinylic double bond. Furthermore, a good correspondence was found between the amount of iodine removed from the polymer and the content of vinyl groups in the unsaturated terpolymer. $^{13}\text{C-NMR}$ spectrum of copolymer 20 is reported in Fig. 3. It shows all the resonances relevant to an ethylene/propylene copolymer. Moreover, in the olefinic region the signals of the vinyl group can be observed: $\text{C}_1 = 113.9$ ppm, $\text{C}_2 = 143.8$ ppm.

Table 6

Fractionation of an ethylene/propylene/1,3-butadiene copolymer (copolymer **18**) obtained by dehydrohalogenation of an ethylene/propylene/1-iodo-3-butene

Fraction	Solvent	Amount wt%	C_3 wt%	1,3-butadiene wt%
Raw sample ^a	–	100	371.6	1.6
1 ^a	ether/acetone = 50/50	2.2	27.5	4.1
2 ^a	ether/acetone = 90/10	8	37.3	1.7
3	ether	13	40.9	1.6
4	ether/hexane = 80/20	59.8	40.5	1.5
5	hexane	9.5	36.7	1.4
6	heptane	2	34	1.2
7	residual	5.5	37	1.5

^a GPC analysis. $M_w \cdot 10^{-3}$ (g/mol) = 630.0 (peak 1), 22.0 (peak 2) for the raw sample; 2.0 (peak 2) for fraction 1; 290.0 (peak 1), 4.2 (peak 2) for fraction 2.

The viscosity of the copolymers was found to be the same before and after the dehydrohalogenation reaction. Furthermore, the unsaturated copolymers showed the same bimodal distribution of the molecular masses observed before the reaction. This indicates that no degradation of the polymers occurred under the experimental conditions employed.

Copolymer **18** was fractionated, according to the aforementioned method, in order to study the chemical composition distribution, particularly as

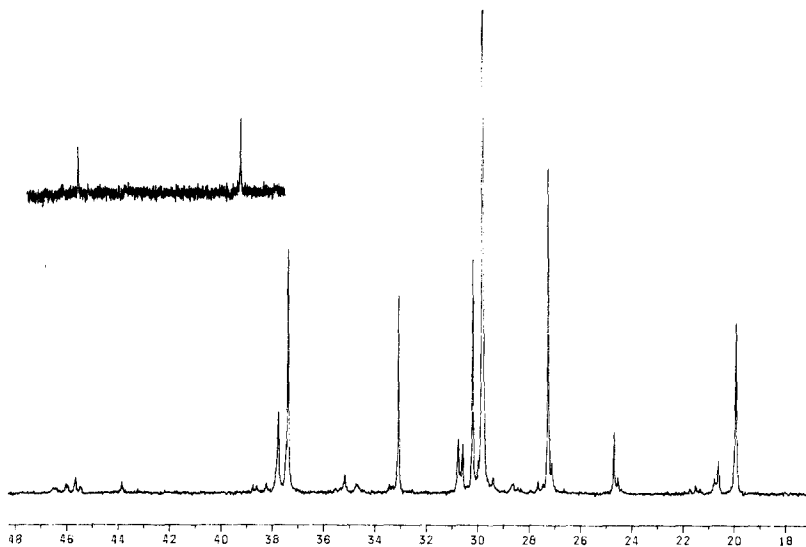


Fig. 3. $^{13}\text{C-NMR}$ spectrum of an ethylene/propylene/1,3-butadiene copolymer (copolymer 20 of Table 5).

far as the unsaturated comonomer is concerned. The results obtained are shown in Table 6. The dehydrohalogenated polymer and the examined fractions showed a bimodal distribution of the molecular masses as the starting iodine containing copolymer. The unsaturated comonomer was homogeneously distributed in the largest part of the copolymer, as already observed for 1-iodo-3-butene in the starting copolymer. These findings confirm that no degradation of the copolymer occurred during the dehydrohalogenation reaction.

The results reported demonstrate that the new method presented in this paper allows the preparation of polyolefins containing polar groups with remarkable efficiency and selectivity, at least as far as polyolefins containing unsaturations are concerned. The data already collected on the preparation of polyolefins containing different polar groups confirm this assertion. Work is in progress to fully characterize these polymers. The paper is soon to be submitted for publication [13].

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