(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 June 2004 (10.06.2004)

PCT

(10) International Publication Number
WO 2004/048424 A1

(51) International Patent Classification[7]: C08F 210/08, C08L 23/02, C08F 4/656

(21) International Application Number: PCT/EP2003/012233

(22) International Filing Date: 3 November 2003 (03.11.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

02080012.4	28 November 2002 (28.11.2002)	EP
60/431,804	9 December 2002 (09.12.2002)	US

(71) Applicant *(for all designated States except US)*: **BASELL POLIOLEFINE ITALIA S.P.A.** [IT/IT]; Via Pergolesi, 25, I-20124 Milano (IT).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **MORINI, Giampiero** [IT/IT]; Via Giotto, 36, I-35100 Padova (IT). **PIEMONTESI, Fabrizio** [IT/IT]; Vicolo Mozzo della Vittoria, 2, I-44100 Ferrara (IT). **VITALE, Gianni** [IT/IT]; Via Fulvio Testi, 22, I-44100 Ferrara (IT). **BIGIAVI, Daniele** [IT/IT]; Via G. Rocchi, 2, I-40137 Bologna (IT). **PELLICONI, Anteo** [IT/IT]; Via Volta, 22, I-45030 Occhiobello (IT). **GARAGNANI, Enea** [IT/IT]; Viale Mons. Natale Mosconi, 75, I-44100 Ferrara (IT). **BAITA, Pietro** [IT/IT]; Via delle Rose, 13, I-45030 S. Maria Maddalena (IT).

(74) Agents: **COLUCCI, Giuseppe** et al.; Basell Poliolefine Italia S.p.A., Intellectual Property, P.le G. Donegani, 12, I-44100 Ferrara (IT).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:
— *of inventorship (Rule 4.17(iv)) for US only*

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BUTENE-1 COPOLYMERS AND PROCESS FOR THEIR PREPARATION

(57) Abstract: The present invention relates to butene-1 copolymers containing up to 40% by mol of ethylene and/or propylene derived characterized by the following properties: d) Product of the reactivity ratios r1·r2≤2; e) Content of butene-1 units in form of isotactic pentads (mmmm)>98%; and f) absence of 4,1 insertions of butene units.

WO 2004/048424 A1

TITLE:

BUTENE-1 COPOLYMERS AND PROCESS FOR THEIR PREPARATION

The present invention relates to butene-1 copolymers containing up to 40% by mol of ethylene and/or propylene derived units, and to a process for their preparation.

Butene-1 copolymers are well known in the art and have a wide range of applicability. In particular, butene-1 copolymers with a low content of comonomer (1-3%by mol) are generally characterized by good properties in terms of pressure resistance, creep resistance, impact strength and can be used in the manufacture of pipes for replacing the metal pipes. One of the key aspects for their application in the pipe sector is the excellent balance between flexibility and rigidity that they must have in order to combine easy pipe workability and mechanical resistance. In addition, butene-1 copolymers with a higher content of comonomer can be used for example as components of blends with other polyolefin or polymeric products, in order to modulate particular properties such as sealing strength, flexibility and softness of the plastic materials.

The butene-1 copolymers can be prepared by copolymerizing butene-1 in the presence of $TiCl_3$-based catalyst components together with diethylaluminum chloride (DEAC) as cocatalyst. The copolymers obtained by this process, however, generally do not show satisfactory properties because of the substantially non-random distribution of the comonomer in the polymer chain. Furthermore, in view of the low yields obtainable with the $TiCl_3$ based catalysts, the butene-1 copolymers prepared with these catalysts have a high content of catalyst residues (generally more than 300 ppm of Ti) which lowers the properties of the polymers making it necessary a deashing step.

Butene-1/propylene copolymers and a method for their preparation are described in EP-A-353319. The said copolymers are obtained by polymerizing the monomers in the presence of a stereospecific catalyst comprising a solid component comprising a Ti compound and a phthalate supported on $MgCl_2$; an alkylaluminum compound and a heterocyclic compound, in particular 1,8-cineole, as external electron-donor compound. In EP-A-353318 the same catalyst system was used to prepare butene-1/ethylene copolymers. The descriptions of both patent applications are silent with respect to certain properties of the copolymers such as product of the monomer reactivity ratios and percent of isotactic pentads which have an effect on the flexibility/rigidity balance of the copolymers. The applicant has reproduced the

copolymers disclosed in the cited applications and has found that the balance between the distribution of the comonomer in the polymer chain and the isotacticity is not completely satisfactory.

Butene-1/ethylene copolymers have been disclosed also in PCT/EP 02/06574 by using a catalyst based on metallocene compounds. However, in this kind of copolymers there is the presence of regioerrors due to 4,1 insertions of the butene-1 units. This kind of regioerrors in the polymer chain makes more difficult to tune the comonomer content of the copolymer because a 4,1 insertion can be considered equivalent to two consecutive ethylene units in the polymer chain.

Thus, it would be desirable to find new butene-1 copolymers having a complex of properties making them suitable for the various applications. We have found that this need is satisfied by butene-1 copolymers having a particular balance between isotacticity and distribution of the comonomer together with absence of 4,1 insertions of the butene-1 units.

It is therefore an object of the present invention to provide butene-1 copolymers containing up to 40% by mol of ethylene and/or propylene derived units, characterized by the following properties:

a) Product of the comonomer reactivity ratio $r1 \cdot r2 \leq 2$;

b) Content of butene-1 units in the form of isotactic pentads (mmmm)> 98%; and

c) absence of 4,1 butene unit insertions.

In particular, the copolymers object of the present invention are endowed with the following features:

a) Product of the comonomer reactivity ratio $r1 \cdot r2 \leq 1.5$ and preferably $r1 \cdot r2 \leq 1$

b) Content of butene-1 units in the form of isotactic pentads (mmmm)$\geq$98.5% and preferably $\geq$ 99%; and

c) absence of 4,1 insertions.

Preferably, the content of (mmmm) is >99% in correspondence of $r1 \cdot r2 \leq 1$. Further, the copolymers of the present invention preferably have a Polydispersity Index measured according to the method specified below, ranging from 2 to 15; more preferably ranging from 3 to 10 and in particular in the range 4-8.

The content of ethylene or propylene derived units in the copolymers of the present invention preferably ranges from 0.1 to 35% by mol, more preferably from 0.5 to 30% by mol.

The copolymers having a content of ethylene or propylene lower than about 3% by moles and

in particular lower than 2.5% can be particularly suitable for use in the pipe sector. In this case, ethylene is a preferred comonomer. Butene-1 copolymers having a comonomer content in the range of 2-15% by moles and preferably 3-12%, can be suitable also for the preparation of polymer compositions for use in low seal initiation temperature or fiber applications.

The applicant also observed that the butene-1 copolymers according to the present invention generally become amorphous when their comonomer content, in particular when the comonomer is ethylene, is about 12% by mol or higher. At these value of comonomer content in fact, a melting point is no longer detectable by carrying out thermal analysis. Moreover, the amount of fractions soluble in xylene at 0°C becomes greater than 95%. Said specific copolymers also proved to be very soft as shown by a Shore A value of lower than 70 and in certain cases lower than 50. In view of these properties, these copolymers can be used in particular as components of polymeric compositions for use in applications where a certain level of softness is required.

Therefore, it constitutes a further object of the present invention a polymer composition comprising:

(A) from 1 to 99% by weight of the copolymer object of the present invention; and

(B) from 99% to 1% by weight of another polymeric component;

said percentages being based on the sum of (A)+(B).

In particular, (A) can be present in an amount ranging from 10 to 90% and (B) in an amount ranging from 90% to 10%. Preferably the component (B) comprises an olefin (co)polymer. In particular the component (B) can be selected from ethylene containing (co)polymers, propylene containing (co)polymers and from their mixtures.

Particularly interesting are the polymer compositions comprising:

(A) from 5 to 40%wt of the butene-1 copolymers of the present invention having from 1 to 15%by mol of ethylene or propylene; and

(B) from 60 to 95%wt of a propylene copolymer containing from 1 to 30 % by mol of ethylene and/or an α-olefin of formula CH_2=CHR, where R is a C2-C10 hydrocarbon group; said percentages being based on the sum of (A)+(B).

Preferably, said α-olefin is butene-1. Particularly interesting are the compositions in which (B) is selected from (a) a propylene copolymer containing both ethylene and butene-1 wherein the content of ethylene is from 1 to 10% and the content of butene-1 is from 1 to 10% and (b) a propylene copolymer containing from 2 to 15% by mol of butene-1.

Said compositions, which are particularly useful in applications where a low seal initiation temperature (SIT) is required, show better performances, in terms of SIT and mechanical properties, with respect to the compositions in which butene-1 copolymers of the prior art are used.

Interesting results have also been obtained by using the copolymers of the invention in the preparation of polymer compositions to be used in applications requiring a specific range of peel force between two layers that have been previously sealed (Seal-Peel applications). Generally, these formulations comprise:

(i) from 5 to 25% wt of the butene-1 copolymer of the invention and

(ii) from 75 to 95%wt of an ethylene polymer; said percentages being based on the sum of (i)+(ii).

The ethylene polymer can be an ethylene homopolymer or copolymer. In particular, it can be selected from branched ethylene homo or copolymers obtained through high pressure high temperature radical initiated polymerization (LDPE), linear ethylene homo or copolymers with alpha-olefins having from 4 to 10 carbon atoms (HDPE or LLDPE) obtained through the use of the well known coordination catalysts such as the Ziegler-Natta catalysts or mixtures thereof.

Also in this case the compositions containing the copolymers of the invention have shown better performances, in terms of peel performances, with respect to the compositions in which butene-1 copolymers of the prior art are used.

The butene-1 copolymers of the present invention can be prepared by polymerization of the monomers in the presence of a stereospecific catalyst comprising (A) a solid component comprising a Ti compound and an internal electron-donor compound supported on $MgCl_2$; (B) an alkylaluminum compound and, optionally, (C) an external electron-donor compound.

Magnesium dichloride in active form is preferably used as a support. It is widely known from the patent literature that magnesium dichloride in active form is particularly suited as a support for Ziegler-Natta catalysts. In particular, USP 4,298,718 and USP 4,495,338 were the first to describe the use of these compounds in Ziegler-Natta catalysis. It is known from these patents that the magnesium dihalides in active form used as support or co-support in components of catalysts for the polymerization of olefins are characterized by X-ray spectra in which the most intense diffraction line that appears in the spectrum of the non-active halide is diminished in intensity and is replaced by a halo whose maximum intensity is displaced towards lower

angles relative to that of the more intense line.

The preferred titanium compounds used in the catalyst component of the present invention are $TiCl_4$ and $TiCl_3$; furthermore, also Ti-haloalcoholates of formula $Ti(OR)_{n-y}X_y$, where n is the valence of titanium, X is halogen, preferably chlorine, and y is a number between 1 and n, can be used.

The internal electron-donor compound is preferably selected from esters and more preferably from alkyl, cycloalkyl or aryl esters of monocarboxylic acids, for example benzoic acids, or polycarboxylic acids, for example phthalic or succinic acids, the said alkyl, cycloalkyl or aryl groups having from 1 to 18 carbon atoms. Examples of the said electron-donor compounds are diisobutyl phthalate, diethylphtahalate and dihexylphthalate. Generally, the internal electron donor compound is used in molar ratio with respect to the $MgCl_2$ of from 0.01 to 1 preferably from 0.05 to 0.5.

The preparation of the solid catalyst component can be carried out according to several methods.

According to one of these methods, the magnesium dichloride in an anhydrous state and the internal electron donor compound are milled together under conditions in which activation of the magnesium dichloride occurs. The so obtained product can be treated one or more times with an excess of $TiCl_4$ at a temperature between 80 and 135°C. This treatment is followed by washings with hydrocarbon solvents until chloride ions disappeared. According to a further method, the product obtained by co-milling the magnesium chloride in an anhydrous state, the titanium compound and the internal electron donor compound is treated with halogenated hydrocarbons such as 1,2-dichloroethane, chlorobenzene, dichloromethane etc. The treatment is carried out for a time between 1 and 4 hours and at temperature of from 40°C to the boiling point of the halogenated hydrocarbon. The product obtained is then generally washed with inert hydrocarbon solvents such as hexane.

According to another method, magnesium dichloride is pre-activated according to well known methods and then treated with an excess of $TiCl_4$ at a temperature of about 80 to 135°C which contains, in solution, an internal electron donor compound. The treatment with $TiCl_4$ is repeated and the solid is washed with hexane in order to eliminate any non-reacted $TiCl_4$.

A further method comprises the reaction between magnesium alcoholates or chloroalcoholates (in particular chloroalcoholates prepared according to U.S. 4,220,554) and an excess of $TiCl_4$ comprising the internal electron donor compound in solution at a temperature of about 80 to

120°C.

According to a preferred method, the solid catalyst component can be prepared by reacting a titanium compound of formula $Ti(OR)_{n-y}X_y$, where n is the valence of titanium and y is a number between 1 and n, preferably $TiCl_4$, with a magnesium chloride deriving from an adduct of formula $MgCl_2 \bullet pROH$, where p is a number between 0,1 and 6, preferably from 2 to 3.5, and R is a hydrocarbon radical having 1-18 carbon atoms. The adduct can be suitably prepared in spherical form by mixing alcohol and magnesium chloride in the presence of an inert hydrocarbon immiscible with the adduct, operating under stirring conditions at the melting temperature of the adduct (100-130°C). Then, the emulsion is quickly quenched, thereby causing the solidification of the adduct in form of spherical particles. Examples of spherical adducts prepared according to this procedure are described in USP 4,399,054 and USP 4,469,648. The so obtained adduct can be directly reacted with the Ti compound or it can be previously subjected to thermal controlled dealcoholation (80-130°C) so as to obtain an adduct in which the number of moles of alcohol is generally lower than 3 preferably between 0,1 and 2,5. The reaction with the Ti compound can be carried out by suspending the adduct (dealcoholated or as such) in cold $TiCl_4$ (generally 0°C); the mixture is heated up to 80-130°C and kept at this temperature for 0,5-2 hours. The treatment with $TiCl_4$ can be carried out one or more times. The internal electron donor compound can be added during the treatment with $TiCl_4$. The treatment with the electron donor compound can be repeated one or more times.

The preparation of catalyst components in spherical form is described for example in European Patent Applications EP-A-395083, EP-A-553805, EP-A-553806, EPA-601525 and WO98/44001.

The solid catalyst components obtained according to the above method show a surface area (by B.E.T. method) generally between 20 and 500 m^2/g and preferably between 50 and 400 m^2/g, and a total porosity (by B.E.T. method) higher than 0,2 cm^3/g preferably between 0,2 and 0,6 cm^3/g. The porosity (Hg method) due to pores with radius up to 10.000Å generally ranges from 0.3 to 1.5 cm^3/g, preferably from 0.45 to 1 cm^3/g.

The alkyl-Al compound (B) is preferably chosen among the trialkyl aluminum compounds such as for example triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum. It is also possible to use mixtures of trialkylaluminum's with alkylaluminum halides, alkylaluminum hydrides or alkylaluminum sesquichlorides such as $AlEt_2Cl$ and $Al_2Et_3Cl_3$.

The external donors (C) are preferably selected among silicon compounds of formula $R_a^5R_b^6Si(OR^7)_c$, where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R^5, R^6, and R^7, are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms optionally containing heteroatoms. A particularly preferred group of silicon compounds is that in which a is 0, c is 3, b is 1 and R^6 is a branched alkyl or cycloalkyl group, optionally containing heteroatoms, and R^7 is methyl. Examples of such preferred silicon compounds are cyclohexyltrimethoxysilane, t-butyltrimethoxysilane and thexyltrimethoxysilane. The use of thexyltrimethoxysilane is particularly preferred.

The electron donor compound (C) is used in such an amount to give a molar ratio between the organoaluminum compound and said electron donor compound (c) of from 0.1 to 500, preferably from 1 to 300 and more preferably from 3 to 100.

In order to make the catalyst particularly suitable for the polymerization step, it is possible to pre-polymerize said catalyst in a pre-polymerization step. Said prepolymerization can be carried out in liquid, (slurry or solution) or in the gas-phase, at temperatures generally lower than 100°C, preferably between 20 and 70°C. The pre-polymerization step is carried out with small quantities of monomers for the time which is necessary to obtain the polymer in amounts of between 0.5 and 2000g per g of solid catalyst component, preferably between 5 and 500 and, more preferably, between 10 and 100g per g of solid catalyst component.

The polymerization process can be carried out according to known techniques, for example slurry polymerization using as diluent a liquid inert hydrocarbon, or solution polymerization using for example the liquid butene-1 as a reaction medium. Moreover, it may also be possible to carry out the polymerization process in the gas-phase, operating in one or more fluidized or mechanically agitated bed reactors. The polymerization carried out in the liquid butene-1 as a reaction medium is highly preferred.

The polymerization is generally carried out at temperature of from 20 to 120°C, preferably of from 40 to 90°C. The polymerization can be carried out in one or more reactors that can work under same or different reaction conditions such as concentration of molecular weight regulator, comonomer concentration, temperature, pressure etc. Working in more than one reactor under different conditions can lead to the preparation of butene-1 copolymers with different average molecular weight in the two reactors and therefore with a broader molecular weight distribution optionally of bimodal type. Moreover, working in more than one reactor under different conditions has the advantage that the various polymerization step can be

properly modulated so as to properly tailoring the properties of the final polymer. This technique has proved to be very effective for solving the operative problems involved with the preparation of the copolymers of the invention with a comonomer content of about 10% by moles or higher. These products in fact, can give problems during certain operations such as pelletization. The applicant has surprisingly found that if the butene copolymer having a final comonomer content of about 10% or higher is obtained through a copolymerization carried out in two or more reactors in series operating under conditions such that in at least one of them is produced a copolymer fraction having a detectable melting temperature, the above operative problems are minimized or fully solved.

In addition, the so obtained products show, for a given total content of comonomer, better mechanical properties, in particular higher tensile strength, with respect to the copolymers having the same total comonomer content but obtained through a single set of polymerization conditions. For example, a butene-1/ethylene copolymer having a total content of ethylene units in the range of 10-25% mol can be advantageously prepared by two polymerization steps under different conditions in which in one of the step is prepared a copolymer having from less than 10% of comonomer for example 1 to 9% while in the other step another copolymer is prepared having a comonomer content higher than 10% and for example in the range 15-40%mol. Depending on the desired kind of properties the skilled in the art can easily adjust the mass balance between the various fractions of the blends in order to have a final content of comonomer that meets the target. The so obtained copolymer can have the same uses as the copolymer obtained via a single set of polymerization conditions. Accordingly, they are particularly suitable for the preparation of polymer compositions for use in applications where a certain level of softness is required.

As mentioned above, the copolymers of the invention are suitable for use in many applications. As a customary routine, for each of these applications the relevant experts can add further polymer components, additives (such as stabilizers, antioxidants, anticorrosives, nucleating agents, processing aids, etc.) and both organic and inorganic fillers which can impart specific properties, without departing from the gist of the invention.

The following examples are given in order to better illustrate the invention without limiting it.

CHARACTERIZATION

Comonomer content

^{13}C-NMR spectra were performed on a polymer solution (8-12 %wt) in dideuterated

1,1,2,2-tetrachloro-ethane at 120°C. The ^{13}C NMR spectra were acquired on a Bruker DPX-400 spectrometer operating at 100.61 MHz in the Fourier transform mode at 120 °C using a 90° pulse, 15 seconds of delay between pulses and CPD (WALTZ16) to remove ^{1}H-^{13}C coupling. About 1000 transients were stored in 32K data points using a spectral window of 60 ppm (0-60ppm).

Butene-Ethylene copolymers

The ethylene content was obtained from the triad distribution ([E] = [EEE]+[EEB]+[BEB]) which is calculated as:

$BBB = (C-2I)/\Sigma$ $BBE = B/\Sigma$ $EBE = L/\Sigma$

$BEB = I/\Sigma$ $BEE = D/\Sigma$ $EEE = (0.25F+0.5G)/\Sigma$

where $\Sigma = (C-2I)+B+L+I+D+(0.25F+0.5G)$.

B, C, D, F, G, I, L are the integrals of the peaks in the ^{13}C NMR spectrum (peak of EEE sequence at 29.9 ppm as reference). The assignment of these peaks are made according to J.C. Randall, *Macromol. Chem Phys.*, *C29*, 201 (1989) and are reported in Table A (nomenclature according to C.J. Carman, R.A. Harrington and C.E. Wilkes, *Macromolecules*, *10*, 536 (1977)).

Table A.

Area	*Chemical Shift*	*Assignments*	*Sequence*
B	37.24	Tβδ	BBE
C	35.20-34.88	Tββ	BBB
	34.88-34.49	Sαγ	BBEB+BEBE
D	34.49-34.00	Sαδ	EBEE+BBEE
F	30.39	Sγδ	BEEE
G	29.9	Sδδ	EEE
I	24.54-24.24	Sββ	BEB
L	11.22	Tδδ	EBE

Butene/propylene copolymers

The propylene content was obtained from the triad distribution ([P] = [PPP]+[PPB]+[BPB]) which is calculated as:

$BBB = M/\Sigma$ $BBP = L/\Sigma$ $PBP = I/\Sigma$

$BPB = 0.5\ D/\Sigma$ $BPP = \frac{1}{3}(A+0.5\ (B+E)+2\ A+B+E)/\Sigma$ $PPP = (C+0.5B)/\Sigma$

Where $\Sigma = M + L + I + 0.5D + \frac{1}{3}(A+0.5\ (B+E)+2\ A+B+E) + (C+0.5B)$ and A, B, C, D, E, I, L, M are the integrals of the peaks in the ^{13}C NMR spectrum (The peak at 27.73 ppm due the CH_2 carbon in the branch of an isotactic BBBBB pentad is used as internal reference). The assignment of these peaks are made according to H.N. Cheng, Journal of Polymer Science, Polymer Physics Edition, **21**, 573 (1983) and are reported in Table B (nomenclature according to C.J. Carman, R.A. Harrington and C.E. Wilkes, *Macromolecules*, *10*, 536 (1977)).

Table B

Area	Chemical Shift	Assignments	Sequence
A	47.15	CH_2 chain	BPPB
B	46.83	CH_2 chain	PPPB
C	46.52	CH_2 chain	PPPP
D	43.67	CH_2 chain	BPBX
E	43.37	CH_2 chain	PPBX
I	28.13	CH_2 branch	PBP
L	27.93	CH_2 branch	BBP
M	27.73	CH_2 branch	BBB

Determination of the product of the reactivity ratios r1xr2

The product of reactivity ratios are obtained from ^{13}C NMR triad distribution according to C.J. Carman, R.A. Harrington and C.E. Wilkes, *Macromolecules*, *10*, 536 (1977) using the following expressions.

Butene/ethylene copolymers:

$$r_1 r_2 = 1 + \left(\frac{[EEE]+[BEE]}{[BEB]} + 1\right) - \left(\frac{[B]}{[E]} + 1\right)\left(\frac{[EEE]+[BEE]}{[BEB]} + 1\right)^{0.5}$$

Butene/propylene copolymers:

$$r_1 r_2 = 1 + \left(\frac{[PPP] + [BPP]}{[BPB]} + 1 \right) - \left(\frac{[B]}{[P]} + 1 \right) \left(\frac{[PPP] + [BPP]}{[BPB]} + 1 \right)^{0.5}$$

Determination of Isotactic Index (mmmm%). by ^{13}C NMR

The assignment of the pentad signals in the region of branch methylene carbons was made according to *Carbon-13 NMR Spectral Assignment of Five Polyolefins Determined from the Chemical Shift Calculation and the Polymerization Mechanism, T. Asakura and others, Macromolecules 1991, 24 2334-2340.*

Due to the superimposition between stereoirregular pentads and peaks from either BBE / EBE or BBP / PBP sequences, the isotacticity of the BBBBB pentad was evaluated from the amount of mrrm pentad (signal at 26.59 ppm) according to the following expression based on the pure "asymmetric bernoullian site" (see *Two-site model analysis of ^{13}C NMR of polypropylene polymerized by Ziegler -Natta catalyst with external alkoxysilane donors, R. Chûjô, Y. Kogure, T.Väänänen, Polymer, 1994, 35, 339-342*):

mmmm% = 100·I(mmmm)/[I(mmmm)+5·I(mrrm)]

Where I(mmmm) is the area of the mmmm signal at 27.73 ppm and I(mrrm) is the area of the single unit error pentad mrrm.

Determination of the percentage of 4,1 inserted butene units

In the case of either butene homopolymers or butene/propylene copolymers the amount of 4,1 inserted butene units is determined via ^{13}C NMR spectroscopy using the above-mentioned experimental conditions. Assignments of 4,1 inserted units are made according to V. Busico, R. Cipullo, A. Borriello, *Macromol. Rapid. Commun. 16*, 269, (1995).

The content of 4,1 insertions is calculated as:

1,4 units = 0.5×Q×100/(Q+B)

Q and B are the integrals of the signals reported in Table B (The peak at 27.73 ppm due the CH_2 carbon in the branch of an isotactic BBBBB pentad is used as internal reference).

Table B

Integral	*Chemical Shift (ppm)*	*Carbon*	*Sequence*
B	40.21	CH_2 ($S_{\alpha\alpha}$)	B
Q	37.3	CH	-CH(CH_2CH_3)-(CH_2)$_5$-CH(CH_2CH_3)-

The percentage of the 4,1 inserted butene units in the case of butene/ethylene copolymers is assumed to be the same as that obtained for the butene-1 homopolymers prepared under identical polymerization conditions apart from the absence of comonomer.

Determination of Polydispersity Index.

This property is strictly connected with the molecular weight distribution of the polymer under examination. In particular it is inversely proportional to the creep resistance of the polymer in the molten state. Said resistance called modulus separation at low modulus value (500 Pa), was determined at a temperature of 200°C by using a parallel plates rheometer model RMS-800 marketed by RHEOMETRICS (USA), operating at an oscillation frequency which increases from 0.1 rad/sec to 100 rad/second. From the modulus separation value, one can derive the P.I. by way of the equation:

$$P.I.:= 54.6*(\text{modulus separation})^{-1.76}$$

in which the modulus separation is defined as:

modulus separation = frequency at G'=500Pa / frequency at G"=500Pa

wherein G' is storage modulus and G" is the loss modulus.

Determination of Shore A

Measured according to ASTM D2240

Tensile Properties

Measured according to ASTM-D638 on a 1.9 mm thick plaque obtained by compression molding (at 200°C with an cooling of 30°/min) of a polymer composition obtained by mixing in a Brabender the relevant copolymer sample with 1% 2,6- di-t-butyl-4-methyl phenol (BHT) at 180°C.

Seal initiation temperature (SIT): determined by preparing 50 .µm-thick films by extruding the compositions of the examples at about 200.degree. C. Each film thus obtained is laid over a plaque of polypropylene having a xylene-soluble of 4% by weight, melt flow rate of 2 g/10 min. The overlapped film and plaque are bonded in a plate-press at 200.degree. C. with a load of 9000 kg. The said load is maintained for 5 minutes. The resulting bonded test pieces are then stretched six times their length and width using a TM LONG film stretcher, thus obtaining films of a thickness of about 20 .mu.m. 5.times.10 cm specimens are obtained from the said films. The sealing values are obtained by applying a 200 g load to heat-sealed samples. For each measurement two of the above specimens are

overlapped with the heat-sealable layers, made up of the compositions of the examples, touching each other. The said overlapped specimens are then sealed along the 5 cm side using a Xentinel combination laboratory sealer model 12-12 AS. The sealing time is 5 seconds, the pressure about 0.12 MPa (1.2 atm) and the width of the seals 2.5 cm. The sealing temperature is increased by 2.degree. C. for each sample to be measured. The sealed samples are then cut to obtain 2.5.times.10 cm strips, whose unsealed ends are attached to a dynamometer, and the minimum seal temperature where the seal does not break when a 200 g load is applied is determined. This temperature represents the seal initiation temperature

Determination of Peel strength

1 Sealing. The film to be tested is cut (MD direction) to samples having a width of 150 mm and a length of 200 mm. Pieces of a 400 μm thick film of the same polymer used for the support layer are cut in the same dimensions, thereby obtaining substrate pieces. Both the samples of films to be tested and the substrate pieces are put between the sealing bars of a KOPP SPGE 20 laboratory sealing machine, with the samples on the top. The upper sealing bar is heated up to the sealing temperature. The sealing bars are closed for 1 second under a pressure of 1.6 bar and seals are produced (100 mm length, 10 mm weld overlap) in the TD direction. The temperatures at which the samples are sealed to the substrate pieces are reported in Table 1.

2. **Peel Test** After conditioning the sealed samples for 24 hours at 23.degree. C., the peel strength is tested with an Instron machine. The samples and the substrate pieces to which they are sealed are first cut to test samples having a width of 15 mm and are then clamped between grips with a grip distance of 50 mm. The force needed to pull open the seal with a constant speed of 50 mm/min. is recorded. Such force, expressed in N/15 mm, corresponds to the peel strength and is reported, for each sample, in Table 1.

EXAMPLES

Preparation of Solid Catalyst Component

Into a 500 ml four-necked round flask, purged with nitrogen, 225 ml of $TiCl_4$ were introduced at 0°C. While stirring, 6.8 g of microspheroidal $MgCl_2 \bullet 2.7C_2H_5OH$ (prepared as described in Ex. 2 of USP 4,399,054 but operating at 3,000 rpm instead of 10,000) were added. The flask was heated to 40°C and 4.4 mmoles of diisobutylphthalate were thereupon added. The temperature was raised to 100°C and maintained for two hours, then stirring was discontinued,

the solid product was allowed to settle and the supernatant liquid was siphoned off.
200 ml of fresh $TiCl_4$ were added, the mixture was reacted at 120°C for one hour then the supernatant liquid was siphoned off and the solid obtained was washed six times with anhydrous hexane (6 x 100 ml) at 60°C and then dried under vacuum. The catalyst component contained 2.8 wt% of Ti and 12.3 wt% of phthalate.

Examples 1-5 Preparation of butene-1/ethylene copolymers

In a 4 liter autoclave, purged with nitrogen flow at 70 °C for one our. 1350 g of butene-1, an amount of ethylene as indicated in table 1 and hydrogen as indicated in table 1 were added. The temperature was raised to nearly 75°C and a pre-reacted mixture containing 75 ml of anhydrous hexane containing 1.4 g of $AliBu_3$, and thexyltrimethoxysilane (Al/ thexyltrimethoxysilane molar ratio of 40) and an amount, indicated in table 1, of solid catalyst prepared as reported above were introduced in nitrogen flow to start the reaction.
The total internal pressure was measured and maintained constant for the whole copolymerization time by continuously feeding ethylene. The amount of ethylene fed in this period is reported in Table 1.
After 2 hours the reaction is stopped by discharging the liquid phase (all the prepared copolymers were completely soluble in 1-butene at 75 °C) in an excess of water.
The copolymer was collected and dried overnight in an oven to remove all traces of water.
The characterization of the copolymers is reported in Table 2. None of the copolymers showed the presence of 4,1-butene units insertion.

Comparative Example 6 Preparation of butene-1/ethylene copolymers

The preparation of the butene-1-ethylene copolymer described in example 2 of EP-A-353318 was repeated. The characterization of the copolymers is reported in Table 2. The copolymer did not show the presence of 4,1-butene units insertion.

Examples 7-10 Preparation of butene-1/propylene copolymers

The copolymerization was carried out according to the procedure described in Example 1 with the only difference that propylene in the amount reported in table 3 was used instead of ethylene. The details regarding the amount of catalyst, the total pressure and the hydrogen used are also indicated in table 1. The characterization of the copolymers is reported in Table 4. None of the copolymers showed the presence of 4,1-butene units insertion.

Examples 11

Preparation of butene-1/ethylene copolymers by sequential copolymerization

The sequential polymerization was carried out in two liquid-phase stirred reactors connected in series in which liquid butene-1 constituted the liquid medium. The same catalyst system described in the previous examples was injected into the first reactor working under the following conditions:

Temperature (°C): 75°C

Ethylene/Butene feed ratio= abt. 5%

Hydrogen/Butene feed ratio= abt 1200 ppm vol

After 2 hours of polymerization the content of the first reactor was transferred into the second reactor where the polymerization continued under the same conditions with the only difference that the ethylene feed was discontinued. The polymerization was stopped after 70 minutes and the final copolymer was characterized. On the basis of the polymerization activity about 70% of the total copolymer was produced in the first polymerization step and showed an ethylene content of 12.2%wt. The remaining 30%, produced in the second reactor, had a calculated ethylene content of 1.6%wt. The ethylene content of the final product is therefore about 9%. The results of the characterization carried out on the final copolymer are reported in Table 5.

Example 12

A five layer film of the type A/B/C/B/A having the following composition was prepared.

(A) Seal/Peel layer (15μm) comprising 65% low density polyethylene having a Melt Index of 1.5 and a density of 0.919; 25% of a linear low density polyethylene (MIE 1; density 0.919) and 15% of the butene-1 copolymer produced as described in Example 1.

(C) Core layer (40 μm) constituted by a linear low density polyethylene (MIE 1; density 0.936)

(B) Backbone layer (15μm) constituted by a low density polyethylene (MIE 0.9; density 0.93)

The film was tested for determination of Peel strength according to the method reported above. The results are shown in Table 6.

Example 13

A mechanical blend comprising 10%bw of the butene-1 copolymer of example 1 and 90% of an isotactic terpolymer having a SIT (Seal Initiation Temperature) of 93°C containing 0.5%wt of ethylene, 18%bw of butene-1 and 81.5% of propylene was prepared. On a film

obtained from this composition was carried out the test for the determination of the SIT that resulted to be 76°C.

Comparison Example 14

A composition as described in the Example 13 was prepared with the only difference that the butene-1 copolymer used was that of comparison example 6. The SIT determined on the film obtained from this composition was 84°C.

Table 1

Ex	Catalyst	P_{total}	Ethylene		Yield
	mg	Bar-g	G [a]	g [b]	Kg/g_{cat}
1	6.5	11.5	3.0	13.4	39.2
2	5.9	11.8	6.0	16.5	22.0
3	5.3	11.9	11.5	39.4	54.7
4	5.8	12.4	20.0	39.0	42.2
5	5.2	13.2	20	53	44.2

a Ethylene added before the injection of the catalyst.
b Ethylene added during the copolymerization in order to keep constant the autoclave pressure.

Table 2

Ex	X.S.[1]	$[\eta]$ [2]	C2-	r_1r_2	Tm	ΔH	Tg	PI	Mmmm	Tens. Strength	Tens. Mod. 23°	Shore A
	%wt	dL/g	Mol%		°C	J/g	°C		%	MPa	MPa	
1	25.0	1.85	2.1	0.8	91.2	19.2	-34	4	99.3	38.3	290	nm
2	96.9	1.75	12.4	0.9	nd-	-	-40	3.9	99.2	14.6	70	75
3	95.6	2.46	19.5	1.0	nd-	-	-42	3.8	99.1	5.8	10.1	45
4	96.2	2.39	29.5	0.9	nd-	-	-46	3.8	99.3	2.6	3.7	29
5	99.2	1.92	34.2	0.94	nd-	-	-	nm	99.3	3.6	7.1	34
6 *	80	1.9	4.3	0.8	nd-	-	-	nm	97.1	30	160	nm

nd = not detectable
nm= not measured
1 Xylene Soluble at 0°C; **2** Intrinsic viscosity in THN;
* Comparative

Table 3

Ex	Catalyst	P_{total}	Propylene		Yield
	mg	Bar-g	G [a]	g [b]	Kg/g_{cat}
7	11.5	12	3.0	50	38.3
8	6.7	12	6.0	26.4	43.3
9	17	13.2	96.3	42.7	42.6
10	11	13.2	96	82.0	40.2

a Ethylene added before the injection of the catalyst.

b Ethylene added during the copolymerization in order to keep constant the autoclave pressure.

Table 4

Ex	X.S.[1]	$[\eta]$ [2]	Propylene	r_1r_2	Tm	ΔH	Tg	mmmm	Tens. Mod. (1-3% chord)
	%wt	dL/g	Mol%		°C	J/g	°C	%	MPa
7	1.2	2.41	0.6	1.2	125	19.2	-34	99.1	286
8	2	1.95	3.3	1.3	124	-	-40	98.6	
9	22	2.25	9.7	1.5	120	-	-42	98.9	
10	97.6	1.7	18.1	1.7	112	-	-46	99.2	200

1 Xylene Soluble at 0°C; 2 Intrinsic viscosity in THN

Table 5

Ex	$^3C2^-$	Tm	ΔH	TS At break	TM23°	Shore A
	Mol%	°C	J/g	MPa	MPa	
11	16.6	90	6	5.6	20	72

CLAIMS

1. Butene-1 copolymers containing up to 40% by mol of ethylene and/or propylene derived units, characterized by the following properties determined by the methods reported in the description:
   a) Product of the reactivity ratios r1•r2 ≤2;
   b) Content of butene-1 units in form of isotactic pentads (mmmm)> 98%; and
   c) absence of 4,1 insertions of butene units.
2. The butene-1 copolymers according to claim 1 in which the content of (mmmm) is >99% in correspondence of r1•r2≤1.
3. The butene-1 copolymers according to claim 1 characterized by the following features:
   a) reactivity ratio r1•r2 ≤1.5;
   b) Content of butene-1 units in the form of isotactic pentads (mmmm)> 98.5%; and
   c) absence of 4,1 insertions.
4. The butene-1 copolymers according to claim 3 having a PI in the range 3-10.
5. The butene-1 copolymers according to claim 1 having a content of ethylene and/or propylene derived units ranging from 0.1 to 35% by mol.
6. The butene-1 copolymers according to claim 5 having a content of ethylene and/or propylene derived units ranging from 0.5 to 30% by mol.
7. The butene-1 copolymers according to claim 6 wherein the comonomer is ethylene.
8. The butene-1 copolymers according to claim 6 wherein the comonomer is propylene.
9. The butene-1 copolymers according to claim 6 having a content of ethylene or propylene lower than about 3%.
10. The butene-1 copolymers according to claim 6 having a content of ethylene and/or propylene in the range of 2-15%.
11. The butene-1 copolymers according to claim 6 having a content of ethylene or propylene derived units equal to, or higher than, 12%.
12. The butene-1 copolymers according to claim 11 in which the comonomer is ethylene.
13. The butene-1 copolymers according to claim 11 characterized by the fact that they do not show a melting point at the thermal analysis.
14. A polymer composition comprising (A) from 1 to 99wt % of a butene-1 copolymer according to claim 1 and (B) from 1 to 99% of another polymeric component the said

percentages being referred to the sum of (A) and (B).

15. A polymer composition according to claim 14 in which the component (B) comprises an olefin (co)polymer.

16. A polymer composition according to claim 14 in which the component (B) is a ethylene containing (co)polymer, a propylene containing (co)polymer or their mixtures.

17. A polymer composition comprising:

(A) from 5 to 40%wt of the butene-1 copolymers according to claim 1 having from 1 to 15%by mol of ethylene or propylene; and

(B) from 60 to 95%wt of a propylene copolymer containing from 1 to 30 % by mol of ethylene and/or an α-olefin of formula CH_2=CHR, where R is a C2-C10 hydrocarbon group.

18. A polymer composition according to claim 17 in which said α-olefin is butene-1.

19. A polymer composition according to claim 18 in which the component (B) is selected from either (a) a propylene copolymer containing both ethylene and butene-1 wherein the content of ethylene is from 1 to 10% and the content of butene-1 is from 1 to 10% or (b) a propylene copolymer containing from 2 to 15% by mol of butene-1.

20. A polymer composition comprising (A) a butene-1 copolymer according to claim 1 not showing a melting point and (B) a butene-1 copolymer according to claim 1 showing a melting point.

21. A polymer composition according to claim 20 in which (A) is a butene-1/ethylene copolymer having a content of ethylene of higher than 10% and (B) is a butene-1/ethylene copolymer having a content of ethylene of less than 10%by mol.

22. A polymer composition comprising :

(i) from 5 to 25% wt of the butene-1 copolymer of the invention and

(ii) from 75 to 95%wt of an ethylene polymer; said percentages being based on the sum of (i)+(ii).

23. Manufactured articles obtained from the butene-1 copolymers or their blends according to any of the preceding claims.

24. Process for the preparation of the butene-1 copolymers according to any of claims 1-13 comprising copolymerizing butene-1 and ethylene and/or propylene in the

presence of a stereospecific catalyst comprising (A) a solid catalyst component comprising a Ti compound and an electron-donor compound selected from phthalates, supported on $MgCl_2$; (B) an alkylaluminum compound and, (C) an external electron-donor compound of formula $R_a^5R_b^6Si(OR^7)_c$, where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R^5, R^6, and R^7, are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms optionally containing heteroatoms.

25. The process according to claim 24 wherein the external donor is thexyltrimethoxysilane.
26. Process according to claim 24 or 25 carried out in liquid butene-1.
27. Process according to claim 26 in which the co-polymerization is carried out in at least two reactors working under different reaction conditions.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/12233

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F210/08 C08L23/02 C08F4/656

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 03/042258 A (BASELL POLYOLEFINE GMBH ; RESCONI LUIGI (IT)) 22 May 2003 (2003-05-22) claims; table 1	1
X	EP 0 172 961 A (MITSUI PETROCHEMICAL IND) 5 March 1986 (1986-03-05)	1-13,23, 24
Y	page 4, line 25 - line 28 page 12, line 17 - line 31 page 17, line 27 - page 18, line 31 example 4; table 1	1-27
Y	EP 0 712 869 A (SHOWA DENKO KK) 22 May 1996 (1996-05-22) page 9, line 9; claims	1-27

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 March 2004	19/03/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Kaumann, E

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/12233

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99/45043 A (MONTELL TECHNOLOGY COMPANY BV) 10 September 1999 (1999-09-10) page 4, line 12 - page 8, line 4 page 9, line 2 - line 4; claim 1	1-27
A	WO 00/63261 A (BALBONTIN GIULIO ; MORINI GIAMPIERO (IT); MONTELL TECHNOLOGY COMPANY B) 26 October 2000 (2000-10-26) page 9 - page 10; claims	1-27
A	EP 0 640 624 A (SHOWA DENKO KK) 1 March 1995 (1995-03-01) the whole document	1-27

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/12233

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03042258 A	22-05-2003	WO 03042258 A1	22-05-2003
EP 0172961 A	05-03-1986	EP 0172961 A1	05-03-1986
		AT 38044 T	15-11-1988
		DE 3474673 D1	24-11-1988
EP 0712869 A	22-05-1996	WO 9531490 A1	23-11-1995
		AU 706739 B2	24-06-1999
		AU 5290798 A	07-05-1998
		AU 690907 B2	07-05-1998
		AU 6561094 A	05-12-1995
		BR 9402947 A	01-06-1999
		DE 69412266 D1	10-09-1998
		DE 69412266 T2	11-02-1999
		EP 0712869 A1	22-05-1996
		US 5916990 A	29-06-1999
		US 6323298 B1	27-11-2001
WO 9945043 A	10-09-1999	AU 744327 B2	21-02-2002
		AU 3143199 A	20-09-1999
		BR 9904849 A	25-07-2000
		CA 2289026 A1	10-09-1999
		CN 1256698 T	14-06-2000
		DE 69910511 D1	25-09-2003
		WO 9945043 A1	10-09-1999
		EP 0980396 A1	23-02-2000
		ID 23020 A	30-12-1999
		JP 2001523302 T	20-11-2001
		NO 995386 A	04-11-1999
		TR 9902698 T1	23-10-2000
		US 6306996 B1	23-10-2001
WO 0063261 A	26-10-2000	AU 4548600 A	02-11-2000
		BR 0006095 A	20-03-2001
		CA 2334743 A1	26-10-2000
		CN 1313869 T	19-09-2001
		WO 0063261 A1	26-10-2000
		EP 1088009 A1	04-04-2001
		HU 0103083 A2	28-11-2001
		ID 28200 A	10-05-2001
		JP 2002542347 T	10-12-2002
		NO 20006388 A	29-01-2001
		PL 345209 A1	03-12-2001
EP 0640624 A	01-03-1995	JP 2879391 B2	05-04-1999
		JP 5287019 A	02-11-1993
		US 5407883 A	18-04-1995
		EP 0640624 A1	01-03-1995
		DE 69311721 D1	24-07-1997
		DE 69311721 T2	13-11-1997
		US 5693729 A	02-12-1997