Investigation of Polymerizability of ω-Alkenyldioxolanes with α-Olefins and Alkyl Vinyl Ethers by Modified Ziegler–Natta Catalysts

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SYNOPSIS

Results are presented of an investigation on the polymerizability of functional olefins, such as allylisopropylidene glycerol (AIPG) and undecenylisopropylidene glycerol (UIPG), in the presence of conventional and modified Ziegler–Natta catalysts based on $TiCl_4$ or $MgCl_2$-supported titanium and triisobutylaluminum, hexaisobutyltetraalumoxane, or bisdiethylaluminum sulfate. Homopolymerization experiments were performed on AIGP at temperatures of −78, 25, and 50°C; only those at 50°C provided appreciable amounts of polymeric materials insoluble in methanol, whose structures comprise monomeric units derived from opening both dioxolane rings and vinyl double bonds. In spite of all attempts and precautions, polymerization experiments carried out on mixtures of the functional olefins AIPG and UIPG with either 4-methyl-1-pentene or isopropyl vinyl ether gave rise to the homopolymers of the nonfunctional α-olefin and of the vinyl ether, without any appreciable amount of either copolymers or homopolymers of the dioxolane containing monomers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

At present, many efforts are being devoted to the production and manufacture of new polymeric materials with lifetimes and performances tailored to comply with stringent environmental regulations. In particular, polyolefins modified by insertion of functional comonomers are expected to have superior dyeability, improved compatibility in blends, and better biodegradability. However, olefin monomers containing functional groups not conjugated to the double bond do not polymerize by radical initiation while interactions with functional groups tend to deactivate catalyst active sites of Ziegler–Natta type systems.[1-4] Much work has been done either to eliminate or at least minimize these interactions; and the results obtained in these investigations indicate that this can be attained by: placing the double bond well apart from the functional group; increasing the steric hindrance around the

heteroatoms; and precomplexation of functional monomers with an organometallic compound or of the organometallic components of the catalyst with aprotic Lewis bases.[5-18]

Recently, the synthesis and polymerization of monoglycidyl ethers of polyols protected by isopropylidene groups were investigated.[19-23] These monomers have great potential for the preparation of polymers with a tunable hydrophilic/hydrophobic balance, even though their use is restricted to ring opening polymerization processes. It seemed therefore useful to prepare two new monomers, namely (R)(S)-2,2-dimethyl-4-allyloxymethyl-1,3-dioxolane (AIPG) and (R)(S)-2,2-dimethyl-4-(10-undecenyl-1-oxymethyl)-1,3-dioxolane (UIPG), containing both a vinyl group and one dioxolane ring separated by one and nine methylene groups, respectively. Structurally these compounds can be considered as monomeric synthons of functional poly(α-olefin)s containing free hydroxyl groups in the side chains, as the protecting isopropylidene group can be quantitatively removed under mild acidic conditions.

In the present article we report the results of an investigation on the homopolymerization and co-

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polymerization of these dioxolane-containing α-olefins with vinyl monomers in the presence of conventional and modified Ziegler–Natta catalysts. The rationale behind this approach was that the use of bulky isopropylidene protecting groups and a long polymethylene spacer could limit the extent of interaction between the monomer heteroatoms and catalytic sites. Moreover, the modified Ziegler–Natta type catalysts we used have been shown to be active in the polymerization of olefins[24,25] and could be less sensitive to the presence of heteroatoms, because the organometallic component used in the catalyst formulation already contained heteroatoms such as oxygen and sulfur.[26-28]

EXPERIMENTAL

Commercial Monomers and Solvents

4-Methyl-1-pentene (4MP) and n-heptane (Fluka) were distilled over Na/K alloy under dry nitrogen atmosphere. Isopropyl vinyl ether (IPVE) was prepared by vinylation of isopropanol with acetylene and distilled prior the use after prolonged stirring on Na-K alloy.[29]

Catalysts

Commercial grade (Schering) triisobutylaluminum (TIBA) and hexaisobutyltetraalumoxane (HIBAO) were used as received. Bisdiethylaluminum sulfate (DEAS) was prepared as previously reported.[24,30]

Commercial grade titanium tetrachloride (Erba) was distilled under dry nitrogen atmosphere. $MgCl_2$-supported titanium catalyst (BO200), having chemical composition $TiMg_{13}Al_{1.5}Cl_{31}$, was supplied by Dr. F. Masi (Enichem Polimeri, Bolgiano–Milan).

AIPG

A solution of 70.0 g (0.53 mol) of isopropylidene glycerol and 1.93 g (6 mmol) of tetrabutylammonium bromide in 70 mL of toluene and 70 mL of 50% NaOH water solution were placed in a 500-mL flask equipped with dropping funnel, reflux condenser, and mechanical stirrer, then 69.9 g (0.58 mol) of allyl bromide were slowly added under vigorous stirring over 6 h. The stirring was continued for 18 h, then the organic layer was washed with water to neutrality and finally dried over anhydrous sodium sulfate. After removal of volatile products the residue was stirred over Na/K alloy for 12 h and then distilled under vacuum to yield 75.6 g (85%) of colorless

liquid product with a boiling point (bp) of 61°C/0.8 mm that was characterized by IR and NMR spectroscopy.

IR (LIQUID FILM): $\bar{\nu}$ = 3100–3000 (ν CH=), 3000–2800 (ν CH aliphatic), 1668 (ν C=C), 1456 (δ CH_2 and δ_{as} CH_3), 1376 (δ_s CH_3), 1250–1000 (ν C—O—C), and 980 and 926 cm^{-1} (δ CH=).

^{1}H-NMR (CDCl$_3$): δ = 1.3 and 1.4 (2 s, 6H, CH$_3$), 3.5 (2 d, 2H, =C—CH$_2$—O), 3.7–4.1 (2 m, 4H, CH$_2$—O), 4.25 (m, 1H, CH—O), 5.15–5.3 (2 m, 2H, =CH$_2$), and 5.85 ppm (1 m, 1H, =CH).

UIPG

A solution of 28.8 g (169 mmol) of 10-undecen-1-ol in 50 mL of anhydrous toluene was cooled to −15°C, then 5.6 mL (61 mmol) of PBr$_3$ were added under stirring, while maintaining the temperature at −5°C. The reaction mixture was heated at 80°C for 6 h. Then after cooling at room temperature, the solvent was distilled off under vacuum and the residue was diluted with diethyl ether, washed with a 5% NaOH, and dried overnight on anhydrous CaCl$_2$. After removal of the solvent, the residue was distilled under vacuum to yield 16.1 g (41%) of 1-bromo-10-undecene as a colorless liquid product with a bp of 102°C/ 4 mm.

A solution of 16.1 g (69 mmol) of 1-bromo-10-undecene, 82.7 (69 mmol) of (R)(S)-isopropylidene glycerol and 0.20 g (0.6 mmol) of tetrabutylammonium bromide in 60 mL of anhydrous tetrahydrofuran (THF) was placed in a 250-mL flask equipped with dropping funnel and reflux condenser. Then 7.76 g of powdered KOH were quickly added under magnetic stirring and the stirring was continued at room temperature for a further 15 h and at 60°C for 15 h. After cooling at room temperature, the precipitate was filtered off and washed several times with THF. The organic phase was collected and after removal of the solvent, distilled under vacuum to yield 14.2 g (76%) of colorless liquid having bp of 49°C/2 mm that was characterized by IR and NMR spectroscopy.

IR (LIQUID FILM): $\bar{\nu}$ = 3080 (ν CH=), 3000–2800 (ν CH aliphatic), 1640 (ν C=C), 1460 (δ CH$_2$ and δ_{as} CH$_3$), 1380 (δ_s CH$_3$), 1118 (ν C—O—C), and 1000 and 910 cm^{-1} (δ CH=).

^{1}H-NMR (CDCl$_3$): δ = 0.9–1.7 (m, 20 H, CH$_3$, and CH$_2$), 2.0 (m, 2H, CH$_2$C=), 3.4 (m, 4H, CH$_2$—O), 3.7 and 4.0

Table I   Homo- and Copolymerization of 2,2-Dimethyl-4-(ω-alkenyl)oxymethyldioxolanes (M_1) with 4-Methyl-1-pentene and Isopropyl Vinyl Ether (M_2) in Presence of Different Catalysts

	Comonomers								
	M_2		Catalyst		Molar Ratio				
M_1 Type	Type	(mol %)	Ti Deriv.	Al Deriv.	Al/Ti	Olefin/Al	Temp. (°C)	Conv.[a] (%)	Polymer M_2 (mol %)
AIPG	—	—	$TiCl_4$	TIBA	3.3	9.2	50	18	—
AIPG	—	—	BO200	TIBA	790	1.5	25	4	—
AIPG	—	—	$TiCl_4$	DEAS	13.0	9.3	50	9	—
AIPG	—	—	$TiCl_4$	DEAS	3.3	9.1	−78	2[b]	—
AIPG	—	—	—	DEAS	—	9.1	50	18[c]	—
AIPG	—	—	—	DEAS	—	13.6	−78	4[b]	—
UIPG	—	—	BO200	TIBA	790	1.5	25	1	—
AIPG	4MP	64	BO200	TIBA	79.0	12.6	25	6	> 98
UIPG	4MP	65	BO200	TIBA	79.0	12.6	25	3	> 98
—	4MP	100	$TiCl_4$	DEAS	3.4	9.0	25	80	100
AIPG	IPVE	50	$TiCl_4$	HIBAO	3.3	9.1	25	23	> 95
AIPG	IPVE	50	$TiCl_4$	DEAS	3.3	9.1	25	11	> 95
—	IPVE	100	$TiCl_4$	HIBAO	3.3	9.0	25	57	100
—	IPVE	100	$TiCl_4$	DEAS	3.4	8.9	25	56	100

In 15 mL of n-heptane at 25°C for 112 days, M_1 + M_2 = 10–30 mmol.
[a] Evaluated as (polymer weight/comonomer weight) × 100.
[b] Duration 5 h.
[c] Duration 2 days.

(2 dd, 2H, dioxolane CH_2—O), 4.3 (m, 1H, CH—O), 4.8–5.0 (m, 2H, =CH_2), and 5.6–5.9 ppm (m, 1H, CH=).

Polymerization Experiments

Polymerization experiments were performed according to a common procedure. Data relevant to individual runs are summarized in Tables I and II,

whereas some typical experiments are herewith described in detail.

Homopolymerization of AIPG in Presence of System Based on TIBA and TiCl₄

A solution of 0.52 g (2.6 mmol) of TIBA in 20 mL of n-heptane was introduced under dry nitrogen atmosphere in a 50-mL glass vial. Then 149 mg (0.79 mmol) of $TiCl_4$ and, after 10-min aging, 4.13 g (24

Table II   Homo- and Copolymerization of 4-Methyl-1-pentene (4MP) with AIPG under Different Experimental Conditions

Run	AIPG (mmol)	4MP (mol %)	Catalyst (Type)	Molar Ratio Al/Ti	Mode[a]	Time (h)	Conv.[b] (%)	4MP[c] (mol %)
AM5	24	67	TIBA/$TiCl_4$	3.3	I	72	2	> 98
AM6	24	67	TIBA/$TiCl_4$	3.3	II	72	9	90
M22	—	100	TIBA/$TiCl_4$	3.3	—	1	2	100
AM7	18	67	DEAS/$TiCl_4$	13.0	I	72	3	> 98
AM8	18	67	DEAS/$TiCl_4$	13.0	II	72	6	96
M23	—	100	DEAS/$TiCl_4$	13.0	—	1	4	100
M25	—	100	DEAS/$TiCl_4$	3.3	—	80	63	100

[a] 4MP was added to a catalyst suspension in 25 mL of n-heptane at 50°C. Then after 60 min AIPG was added to the polymerization mixture either altogether (mode I) or dropwise over 30 min (mode II). Molar ratio monomers/Ti = 30.
[b] Evaluated as (polymer weight/comonomer weight) × 100.
[c] 4MP content of the polymeric product as evaluated by ^{1}H-NMR.

mmol) of AIPG were added under stirring. The vial was heated under vigorous stirring at 50°C for 2 days. The mixture was poured into 250 mL of ethanol containing 1 g of NH_4Cl and the coagulated product, washed several times with ethanol, and dried under vacuum to yield 0.74 g (conv. 18%) of a semisolid polymeric product that was characterized by GPC analysis and IR and NMR spectroscopy.

Homopolymerization of AIPG at −78°C in Presence of DEAS

A solution of 2.07 g (12 mmol) of AIPG in 15 mL of n-heptane was placed under dry nitrogen atmosphere in a 50-mL glass vial. After cooling at −78°C, 0.5 mL (0.44 mmol) of a 0.87M toluene solution of DEAS was added. The mixture was kept under stirring at −78°C for 5 h and then poured in 250 mL of ethanol containing 1 g of NH_4Cl. The coagulated product, washed several times with ethanol, was dried under vacuum to yield 0.29 g (conv. 14%) of white polymeric product that was characterized by GPC analysis and IR and NMR spectroscopy.

Copolymerization of AIPG and 4MP in Presence of System Based on TIBA and MgCl₂ Supported Titanium Catalyst

A solution of 0.19 g (0.96 mmol) of TIBA in 20 mL of n-heptane was introduced under dry nitrogen atmosphere in a 50-mL glass vial. Then 0.7 mL (12 μmol of Ti) of a 17.4 mM toluene solution of BO200 and, after 10 min aging, 0.66 g (7.8 mmol) of 4MP and 0.74 g (4.3 mmol) of AIPG were added under stirring. The vial was stirred at 25°C for 112 days, then the mixture was poured into 250 mL of ethanol containing 1 g of NH_4Cl. The coagulated product, washed several times with ethanol, was dried under vacuum to yield 80 mg (conv. 6%) of a white polymeric product that was characterized by GPC analysis and IR and NMR spectroscopy.

Copolymerization of AIPG and IPVE in Presence of System Based on DEAS and TiCl₄

n-Heptane, 15 mL, and 2.6 mL (2.0 mmol) of a 0.77M toluene solution of DEAS were introduced under dry nitrogen atmosphere in a 50-mL glass vial, then 0.22 g (1.2 mmol) of $TiCl_4$ were added and the resulting suspension was heated at 50°C for 10 min. After cooling at room temperature, 3.7 g (17.5 mmol) of AIPG and 1.5 g (17.5 mmol) of IPVE were added under stirring. The vial was constantly stirred at 25°C for 112 days, then the mixture was poured into 250 mL of ethanol containing 1 g of NH_4Cl and the coagulated

product. This was washed several times with ethanol and dried under vacuum to yield 0.56 g (conv. 11%) of a white polymeric product that was characterized by GPC analysis and IR and NMR spectroscopy.

Characterization of Polymerization Products

Viscometric measurements were made on solutions at different concentrations of polymer either in chloroform at 30°C or in decalin at 135°C, by using a Desreux–Bishoff dilution viscometer.

GPC analyses were performed on polymer solutions in THF by a Perkin–Elmer model 2/2 liquid chromatograph equipped with UV and RI detector. Polystyrene standards were used for calibration.

IR spectra were recorded on liquid films, KBr pellets, and polymer cast films by a Perkin–Elmer 1600 FTIR spectrophotometer. NMR spectra were recorded on a Varian Gemini 200 spectrometer in 5-mm tubes on 5% (w/v) solutions in perdeuterated solvents or in 9 : 1 mixtures of 1,2,4-trichlorobenzene (TCB)/C_6D_6. ^{1}H-NMR spectra were recorded at 200 MHz. Spectral conditions were as follows: size, 11,968 points; spectral width, 3 kHz; pulse, 30°; acquisition time, 2 s; number of scans, 1. ^{13}C-NMR spectra were recorded at 50.3 MHz under conditions of full proton decoupling. Spectral conditions were as follows: size, 23,936 points; spectral width, 15 kHz; pulse, 70°; relaxation delay, 1 s; acquisition time, 0.8 s; number of scans, 40,000. No weighing function was applied before the Fourier transformation.

RESULTS AND DISCUSSION

Homopolymerization of Alkenyldioxolanes

The polymerizability of AIPG and UIPG was investigated in the presence of Ziegler–Natta type catalysts obtained by reacting an organoaluminum derivative, such as TIBA, HIBAO, or DEAS, with either $TiCl_4$ or MgCl₂-supported titanium catalyst (BO200) that has been found to be particularly active in the polymerization of ethylene and propylene.[31]

4MP   IPVE   AIPG

UIPG
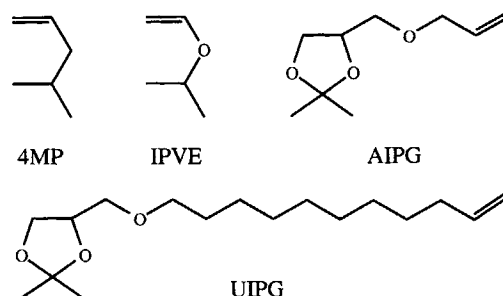
Homopolymerization experiments were carried out in n-heptane at 25 and 50°C, respectively, for 112 and 2 days, by using molar ratios of monomer/Al $\approx$ 10 and Al/Ti = 3.3 and 790 when TiCl$_4$ and BO200 were employed. In runs carried out at 25°C (Table I), the DEAS/TiCl$_4$ catalytic system, which is barely active at room temperature,[24,25] was activated by heating at 50°C for 10 min.

Independent of the catalysts used, no methanol insoluble polymer was formed in almost all runs performed at 25°C; at 50°C between 4 and 18% of medium–low molecular weight polymers ($\bar{M}_w$ 3000–7000 and $\bar{M}_w/\bar{M}_n \approx 5$) were produced.

IR, ^{1}H-NMR, and ^{13}C-NMR spectra of the polymerization products were quite complex and did not allow an easy assignment of definite structures. However, the presence of signals relevant to both dimethyldioxolane rings and vinyl groups in NMR spectra (Fig. 1) indicated that the polymerization process did not involve the vinyl double bond exclusively but proceeded also by ring opening. It is known that dioxolanes can be polymerized by both protic and Lewis acids to give polyethers (polyacetals) by cationic polymerization.[32,33] No experiments have been reported on the anionic polymerization of 1,3-dioxolanes. This finding deserves further investigation and can be exploited in experiments of hybrid copolymerization.[34]

Runs carried out at −78°C in the presence of the DEAS/TiCl$_4$ system and at −78 and 50°C in the presence of DEAS alone produced oligomers with molecular weight and spectroscopic properties similar to those of the samples obtained at 50°C. The almost complete structural identity of polymers obtained either in the presence or in absence of titanium derivative implies that the observed catalytic activity originates from the organoaluminum derivative rather than from the Ziegler–Natta system.

Copolymerization of Alkenyldioxolanes

Copolymerization reactions of AIPG and UIPG with 4MP and IPVE were investigated to verify whether the presence of an easily polymerizable comonomer could promote the polymerization of alkenyldioxolanes.

Polymerization experiments were carried out in n-heptane at 25°C for 112 days in the presence of the catalytic systems obtained by reacting TIBA, HIBAO, and DEAS with either TiCl$_4$ or with MgCl$_2$-supported titanium catalysts (BO200), using molar alkenyldioxolane/comonomer ratios between 1 and 0.5 (Table I). The DEAS/TiCl$_4$ system was preactivated by heating at 50°C for 10 min.
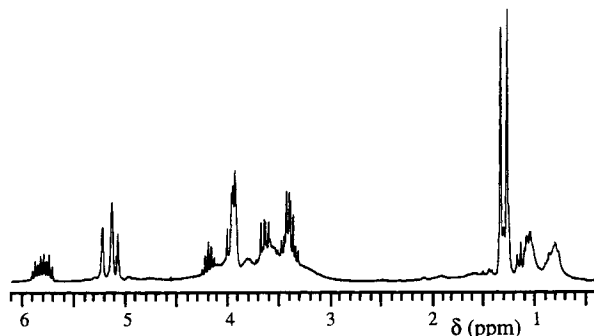
Figure 1 ^{1}H-NMR spectrum of poly(allylisopropylidene glycerol) prepared at 50°C in the presence of the catalytic system based on TiCl$_4$ and TIBA.

No methanol insoluble polymeric product was formed in the copolymerization of alkenyldioxolanes with 4MP in the presence of catalytic systems based on TiCl$_4$.

Rather poor yields (3 and 6%) of polymeric products were obtained in the presence of BO200, a catalyst characterized by an extremely high activity in the anionic-coordinate polymerization of α-olefins.[24,31] However, IR and NMR spectroscopic analyses demonstrated that, within the sensitivity limits of the techniques, the reaction products were exclusively poly(4-methyl-1-pentene). It is worth mentioning that 80% of highly isotactic poly(4MP) was obtained by homopolymerization of 4MP under the same experimental conditions adopted for the copolymerization.

These results not only confirm a rather low tendency of alkenyldioxolane monomers to polymerize in the presence of Ziegler–Natta type catalysts, but also highlight their tendency to inactivate the catalytic sites, thus inhibiting also the polymerization of 4-methyl-1-pentene.

Similarly, copolymerization of AIPG with IPVE under the same experimental conditions afforded low conversions (11 and 23%) to polymeric products constituted solely by IPVE units, as shown by ^{1}H-NMR analysis (Table I). Much higher yields (55%) were observed in the homopolymerization of IPVE, thus substantiating the negative influence of the dioxolane ring on the activity of both conventional and modified Ziegler–Natta catalysts.

To gain a better understanding of the mechanism of catalyst inactivation, copolymerization of AIPG with 4MP was further investigated. Copolymerization runs were carried out in 25 mL n-heptane at 50°C in the presence of the catalytic systems obtained by reacting TiCl$_4$ with either TIBA or DEAS, at molar ratios of comonomers/Ti of 30, Al/Ti of 3.3, and 4MP/AIPG of 2 (Table II). Three different

experiments were performed simultaneously for each organoaluminum derivative: the catalyst obtained by mixing $TiCl_4$ and the organoaluminum compound in n-heptane was activated for 10 min at 50°C and the polymerization was initiated with 4MP. One hour later, one of the experiments was stopped by addition of methanol, whereas in the other two parallel runs AIPG was added all at once (mode I) and dropwise over 30 min (mode II), respectively.

When the functional comonomer was added together with the olefin (runs AM5 and AM7), the exclusive formation of poly(4MP) was observed, with extremely low conversions (2–3%) comparable to those obtained when 4MP homopolymerization was stopped after 1 h (runs M22 and M23). A much higher conversion (63%) to poly(4MP) was achieved when the homopolymerization experiment was continued for 80 h (run M25). When AIPG was added dropwise to the polymerization mixture (runs AM6 and AM8), somewhat larger conversions (6 and 9%) to polymeric products, mainly constituted by 4MP units but containing also 5–10% of units derived from AIPG, were observed.

These results confirm that catalyst active sites are poisoned by the functional comonomer almost instantaneously or more gradually when AIPG is added altogether or dropwise, respectively. Most likely a parasitic reaction of AIPG with the aluminum derivative occurs.[35,36] It seems therefore that significant amounts of copolymerization products containing both monomeric units can be obtained only when the molar functional monomer/aluminum derivative ratio is lower than 1.

CONCLUSIONS

The results of an investigation aimed at the evaluation of the polymerizability of dioxolane-containing α-olefins with the dioxolane moiety either close to (AIPG) or well apart from (UIPG) the vinyl double bond are reported. Homopolymerization and copolymerization experiments with 4-methyl-1-pentene and isopropyl vinyl ether were carried out in the presence of conventional, superactive, and modified Ziegler–Natta catalysts. In spite of all attempts and precautions, in all cases very poor conversions of the dioxolane-containing monomers were attained and a negative interference of the dioxolane ring with the catalyst active sites was evidenced under all experimental conditions. These results furthermore stress the well-known resistance of functional olefins to polymerize by an anionic coordinate mechanism.

Indications were that the dioxolane ring has the tendency to open up and provide polyacetal type polymers bearing a vinyl bond in the side chain. This aspect is worthy of further investigation, because once it is properly controlled, it could open the way to a family of new functional polyethers giving rise to useful postcuring reactions.

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