Pure WCl$_4$-catalyst for polymerization of norbornene and monosubstituted acetylenes

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Abstract

A suspension of commercial WCl$_4$ initiates rapid polymerization of norbornene and norbornadiene under mild conditions. If norbornenyl acetate is used as a substrate, WCl$_4$ is dissolved and homogeneous polymerization occurs. In both cases polymers ($\overline{M}_w$ = about 80 000), the structure of which corresponds to the ring-opening metathesis mode of polymerization, were prepared.

WCl$_4$ has also been found to polymerize monosubstituted acetylenes (benzene, 50°C). Poly(t-butylacetylene) of $\overline{M}_w$ = 600 000, poly(phenylacetylene) of $\overline{M}_w$ = 200 000 and poly(1-hexyne) of $\overline{M}_w$ = 14 000 were prepared in high yields. When WCl$_4$ was dissolved in the reaction with oxygen-containing compounds (e.g. methyl acetate, acetylacetone, acetophenone) before substrate addition, catalyst activity increased significantly. WCl$_4$ in 1,4-dioxane was found to be a very active system for phenylacetylene polymerization; it polymerizes this monomer at the monomer-to-catalyst mole ratio equal to 1000 providing polymer of $\overline{M}_w$ = 400 000.

1. Introduction

In the catalyst systems based on WCl$_6$ (widely used for olefin metathesis and related reactions), reduction of tungsten to the lower oxidation states was postulated to participate in the transformation of WCl$_6$ into the catalytic active species (tungsten carbenes) [1]. This reduction is accomplished by addition of cocatalyst and/or by the substrate itself. For example, Masuda et al. [2] found an average oxidation state of W = IV in active catalyst solution formed from WCl$_6$ and Ph$_4$Sn. Similarly, for ring-opening metathesis polymerization (ROMP) of norbornene

(NBE) by WCl$_6$, WCl$_4$ formed in situ was suggested to be a close precursor of active centres [3]. However, according to our experience, no attempt has been reported to use pure WCl$_4$ directly as catalyst in ROMP and acetylenes polymerization (only a mention is given in the Ref. [4] but without specification of any results). The insolubility of WCl$_4$ in aromatic solvents was probably the main discouragement.

We decided to test the activity of WCl$_4$ in the polymerization of NBE and its derivatives: norbornadiene (NBDE) and 5-norbornen-2-yl acetate (NBEAc) and some monosubstituted acetylenes (Eqs. (1)–(3)). These monomers are known to transform high valent tungsten chlorides (WCl$_6$, WOCl$_4$, WCl$_5$) into the metatheti-

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cally active species without participation of organometallic cocatalyst [5–7].

(1)

P = polymer chain

(2)

(3)
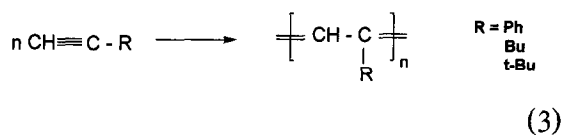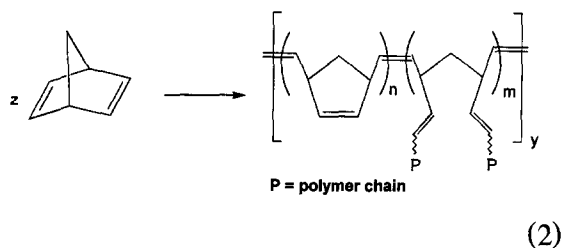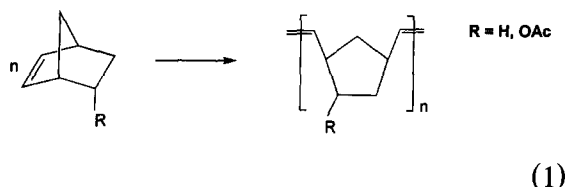
2. Experimental

2.1. Materials

WCl_4 (Aldrich), 97%, used without any purification. Methyl acetate, acetylacetone, epichlorohydrin, acetophenone and 1,4-dioxane (all purum) were purified by conventional methods (i.e. they were distilled, dried, and degassed in vacuo). Norbornene and norbornadiene (both Fluka, purum) were distilled from NaH, 5-norbornen-2-yl acetate (Janssen Chimica, 98% purity, 80% of endo-isomer) was distilled in vacuo, (acidity number was 0.9). Phenylacetylene (Fluka, purum), 1-hexyne (Fluka, purum) and t-butylacetylene (Aldrich, 98%) were dried with NaH and distilled in vacuo. Benzene was purified by H_2SO_4, dried with NaH, distilled and degassed in vacuo. Details are given elsewhere [7,8].

2.2. Procedures

All procedures were carried out under purified Ar or in vacuo using the standard vacuum break-seals technique. Polymers were isolated by precipitation in methanol and dried in vacuo at 40°C. The polymer yields were determined by gravimetry.

2.3. Techniques

IR spectra of polymers (in KBr pellets) were recorded on Specord 75 IR. Molecular weights of polymers were measured by SEC using polystyrene calibration method (Polymer Standard Service). TSP liquid chromatograph system equipped with CM 3200 pump, SM 3200 UV detector working at 254 nm and RI detectors, two columns 300 mm packed with PL-gel (mixed B and mixed C), and THF as the mobile phase (0.7 ml/min) at room temperature were used. The SEC analysis of polyacetylenes were carried out using standard procedure [9] in order to minimize an influence of the polymer degradation on the results obtained [10]. NMR spectra of polymers were measured in CCl_4 on a Varian Unity 500 spectrometer (500 MHz, TMS as an external standard). UV–VIS spectra of the catalyst solutions were recorded on a Hewlett Packard HP 89500 spectrometer using sealed evacuated cuvette.

3. Results

3.1. Polymerization of NBE and its derivatives with WCl_4

The results of the polymerization of NBE, NBEAc and NBDE are given in Table 1. Suspension of commercial WCl_4 initiates polymerization of all these monomers to high polymer yields. In the case of NBE and NBDE, solid phase of tungsten chloride was observed during the whole polymerization process, but if NBEAc was used as a monomer, the insoluble

phase disappeared (and the benzene phase turned red) before the viscosity of the polymerization mixture began to increase. It suggests that in the latter case, WCl_4 was dissolved due to the interaction with ester groups of NBEAc and most probably homogeneous polymerization occurred.

Poly(NBDE) was formed as an insoluble, intractable polymer (probably due to the high cross-linking). Samples of poly(NBE) and poly(NBEAc) were soluble in aromatics (benzene, toluene, chlorobenzene) and THF, weight average molecular weights were about 80 000 and IR spectra of both polymers provided evidence that ROMP really occurred (the presence of the bands corresponding to the double bonds along the main chain: for poly(NBEAc) 973, 755 and 1408 cm^{-1} and for poly(NBE) 966, 740 and 1408 cm^{-1}). The spectra of poly(NBEAc) are identical with those reported for poly(NBEAc) prepared with catalyst systems WCl_6/Me_4Sn [11]. In the case of poly(NBE), however, there is a significant difference in the relative intensities of the IR bands at 966 cm^{-1} (*trans* double bond δ_{CH} vibration) and at 740 cm^{-1} (*cis* double bond δ_{CH} vibration) between polymers prepared with WCl_4 and WCl_6/Me_4Sn, respectively. The ratio of absorbances A_{966}/A_{740} was found to range from 1.6 to 1.8 for poly(NBE)s prepared with WCl_4, whereas to be equal to 2.8 for poly(NBE) prepared using WCl_6/Me_4Sn catalyst (mole ratio $Sn/W = 4$, benzene, 50°C). It indicates higher content of *cis* units in polymers prepared with

WCl_4 in comparison with that prepared using WCl_6/Me_4Sn system.

3.2. Polymerization of monosubstituted acetylenes with WCl_4

Table 2 shows the results of experiments in which phenylacetylene (PhA), *t*-butylacetylene (*t*-BuA) and 1-hexyne were polymerized by suspension of WCl_4 in benzene. In polymerizations using WCl_4 in the presence of oxygen containing compounds, Table 2, the catalyst was dissolved prior to the addition of monomer. WCl_4 was allowed to react with each compound from the following series (mole ratio 1:1, benzene, 50–60°C): methyl acetate (MeOAc), acetylacetone (AcAc), acetophenone (AcPh) and epichlorohydrin (EPCH). These dissolution reactions proceeded relatively slowly, but after several hours the solid phase disappeared and coloured solutions (approximately 0.1M with respect to W) arose. Additionally, WCl_4 was treated with excess of MeOAc and 1,4-dioxane, resp. (without benzene) and brown solutions appeared (about 0.1M with respect to W) after several days at room temperature. All the solutions prepared were stable at least for a week (their UV–VIS spectra, Fig. 1, were not exhibiting any changes within this period).

It is seen from Table 2 that WCl_4 represents an efficient catalyst for polymerization of monosubstituted acetylenes. Its efficiency further increased as a result of WCl_4 reaction with oxygen containing organic compounds given

Table 1

Polymerization of NBE, NBDE and NBEAc with WCl_4 dispersion in benzene, c_0 – initial monomer concentration, t – reaction temperature, $\overline{M}_w$ and $\overline{M}_a$ – weight-average and number-average molecular weight

No.	Monomer	Mole ratio monomer/W	c_0 (mol/l)	t (°C)	Time (h)	Polymer yield (%)	$\overline{M}_w$	$\overline{M}_a$
1	NBE	100	2.7	25	19	25	–	–
2	NBE	100	2.7	50	3	23	–	–
3	NBE	100	4.5	25	19	70	81 000	35 000
4	NBDE	100	4.6	25	19	93	–	–
5	NBEAc [a]	75	3.4	80	2	48	89 000	34 000

[a] WCl_4 dissolved in the reaction mixture.

Table 2

Polymerization of monosubstituted acetylenes with WCl_4 in benzene (if not stated otherwise). c_o = initial concentration of monomer = 4.6 mol/l, benzene, t – reaction time, $\overline{M}_w$ and $\overline{M}_a$ – weight-average and number-average moleculare weight

No.	Monomer	Catalyst	Mole ratio monomer/W	Temperature (°C)	t (h)	Polymer yield (%)	$10^{-3} \times \overline{M}_w$	$10^{-3} \times \overline{M}_a$
1	PhA	WCl_4	100	50	2	44	190	95
2	t-BuA	WCl_4	70	50	2	95	630	250
3	1-hexyne	WCl_4 [a]	100	50	2	44	14	7
4	PhA	WCl_4 + MeOAc	100	50	2	57	200	100
5	PhA	WCl_4 + EPCH	100	50	2	84	180	80
6	PhA	WCl_4 + AcAc	100	50	0.25 [e]	89	125	60
7	PhA	WCl_4 + AcPh	100	25	0.25 [e]	84	112	57
8	PhA	WCl_4 in 1,4-dioxane [b]	100	25	0.25 [e]	92	80	40
9	1-hexyne	WCl_4 in 1,4-dioxane [b]	100	25	2	76	24	11
10	PhA	WCl_4 in MeOAc [c]	100	25	0.25 [e]	84	100	48
11	PhA	WCl_4 in 1,4-dioxane [b]	1000	25	2	70	153	82
12	PhA	WCl_4 in 1,4-dioxane [d]	1000	25	24	25	400	214

[a] Bulk polymerization.
[b] Polymerization in 1,4-dioxane.
[c] Polymerization in benzene/MeOAc = 1/1 (V/V).
[d] Polymerization in benzene /1,4 dioxane = 4:1 (V/V) c_o = 1.5 mol/l.
[e] Extremely viscous solution was formed in a short time after the initiation of polymerization.

above (experiments No. 4, 5, 6, 9). In the case of PhA polymerization, the systems arising from the reaction of WCl_4 with AcPh (1:1) and of WCl_4 with the excess of MeOAc or 1,4-dioxane have been found as very effective, since they provided high polymer yields in several minutes at room temperature (No. 7, 8, 10). In addition, WCl_4 in 1,4-dioxane gave high polymer yield

even at mole ratio PhA/W = 1000, (No. 11) and if diluted with benzene it provided poly(PhA) of very high molecular weight (No. 12).

Poly(t-BuAc) prepared by WCl_4 was white, high molecular weight, tough polymer, poly(1-hexyne)s were orange greasy material. All poly(PhA) samples prepared were orange–red
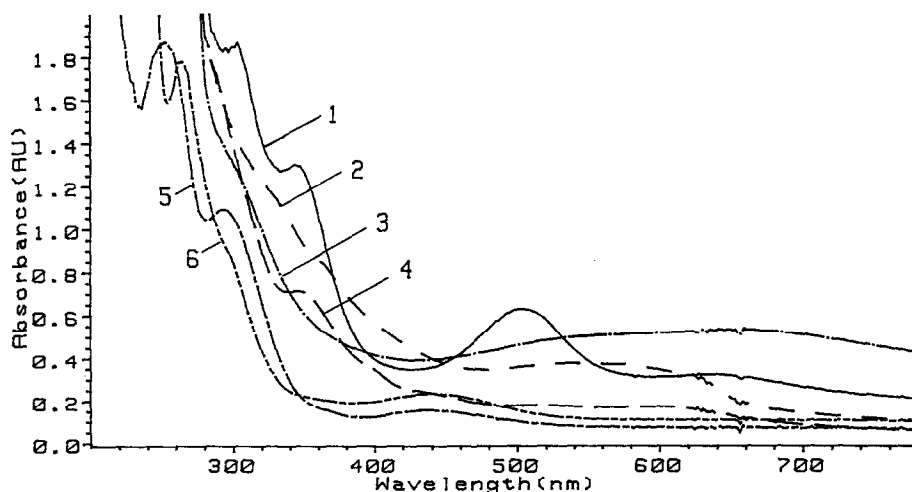

Fig. 1. UV–VIS spectra of catalyst solutions prepared by reaction of WCl_4 with oxygen containing organic compounds. 1 – WCl_4 + MeOAc (1:1) in benzene, 2 – WCl_4 + AcAc (1:1) in benzene, 3 – WCl_4 + EPCH (1:1) in benzene, 4 – WCl_4 + PhAc (1:1) in benzene, 5 – WCl_4 in 1,4-dioxane, 6 – WCl_4 in MeOAc. Diluted solutions (0.001–0.005M), l = 0.1 cm.

solids. Their configurational structure (on the basis of the IR and ^{1}H-NMR spectra) was similar to that of poly(PhA)s prepared by other tungsten catalysts (high *trans* double bond content and low content of units comprised in cyclohexadiene sequences [12]) with exception of poly(PhA)s prepared using WCl_4 in 1,4-dioxane, in which higher content of *cis* double bond was observed (about 80% *cis* junctions using Simionecsu formula [13]). Similar influence of 1,4-dioxane addition to the tungsten based catalyst (the increase of molecular weight and *cis* double bond content of poly(PhA) prepared) has already been observed for $WOCl_4/Ph_4Sn$ system [14,15].

The results presented here show that WCl_4 (either in benzene suspension or dissolved using appropriate compounds) is an effective catalyst for polymerization of norbornene type monomers as well as monosubstituted acetylenes. They support also the suggestion (made earlier [1–3,8]) that W(IV) chloride species, formed in situ from the catalyst systems based on high valent tungsten chlorides, are the closest precursors of catalytic centres for olefin metathesis and acetylenes polymerization.

Acknowledgements

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