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Telechelic oligomers obtained by metathetic degradation of both polyisoprene and styrene–butadiene rubbers. Applications for recycling waste tyre rubber

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ABSTRACT

Metathetic degradation of synthetic cis-1,4-polyisoprene (PI) and styrene–butadiene copolymer (SBR) was performed with cis-1,4-diacetoxy-2-butene (DAB) as chain transfer agent (CTA) using Grubbs II catalyst. Well-defined acetoxy telechelic polyisoprene structures were obtained in a selective manner with a wide range of targeted average molecular weights from 350 g mol^{-1} to 98,000 g mol^{-1}, with a polydispersity index of around 2. Starting from SBR, a similar structure control was obtained with a range of M_n from 1400 g mol^{-1} to 65,000 g mol^{-1}. It was found that precise selection of catalyst concentration and solvent is the major factor to obtain targeted products with high M_n control. Moreover, preliminary tests using such a procedure have shown its efficiency starting from waste tyre. This methodology thus suggests the possibility to recycle such rubber waste leading to high value liquid rubber.

1. Introduction

Olefin metathesis is a metal-catalysed chemical transformation which acts on carbon–carbon double bonds and rearranges them via cleavage and reassembly [1–5]. Inter-molecular metathetic degradation of unsaturated polymers may thus be performed by the addition of a monoolefin and a transition metal carbene complex as catalyst. The polymer backbone is cleaved at the double bonds via transalkylidenation with the added olefin to produce cyclic oligomers and end-functionalized polymers (telechelics) [2]. In order to perform such a reaction, there are several well-defined, single-species catalysts based on different transition metals such as titanium [6], tungsten [7–9], molybdenum [7,10], rhenium [11], osmium [12], and ruthenium [3,13,14] evolved from the original metathesis-active catalyst. More particularly, Grubbs et al. [4] showed that unlike the titanium, tungsten, and molybdenum catalysts, ruthenium-based catalysts react preferentially with olefins over most other species. This gives ruthenium catalysts higher stability towards alcohols, aldehydes, carboxylic acids, and water in contrast to the previous ones. Early articles show that the intra- and inter-molecular metathesis degradation of cis-polybutadiene (cis-PB) and other polyalkenamers may be performed using tungsten, molybdenum and ruthenium-based metathesis catalysts [15–22]. However, although some scientific developments on the metathetic degradation of cis-1,4-polyisoprene and synthetic rubber have been described in the literature [23–27] involving mainly the use of Schrock catalysts [28,29] in organic solvents, there are comparatively few reports concerning the use of Grubbs catalysts for such procedures. Indeed, the difficulties encountered are due to the fact that on one hand PI is very sensitive to side reactions. On the other hand, it has been demonstrated that standard tungsten chloride [30], initiates cationic cyclization as a side reaction. Moreover, PI with tri-substituted unsaturation dramatically decreases the catalyst reactivity meaning that polymer degradation occurs much more slowly when compared with the degradation of polybutadiene [31]. Since ruthenium-based catalysts show a high tolerance to a wide variety of functional groups [13], they widened the choice of end chain functionalities that can be incorporated by the chain transfer agent. As an example, Craig et al. showed that the use of N-heterocyclic carbene ligands leads to the rapid and efficient metathesis degradation of cis-PI [32]. First and second generation ruthenium Grubbs catalysts are currently the most common organometallics used in metathesis. They are demonstrated to display high efficiency in various metathesis reaction types when compared with their predecessors [33–42]. More particularly, the development of the second generation Grubbs catalysts allowed the synthesis of

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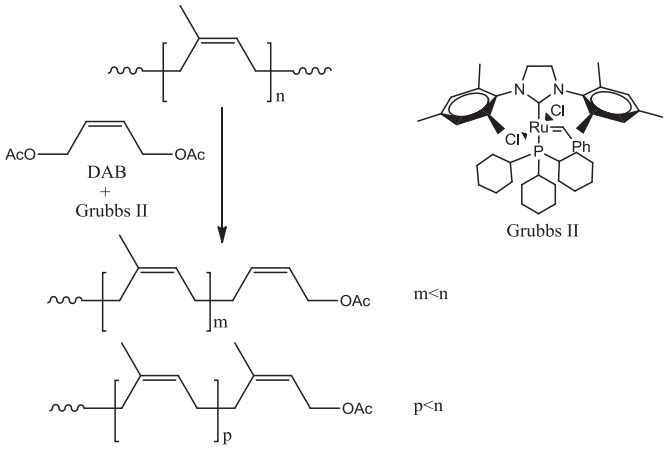

Scheme 1. Structure expected from the metathetic degradation of cis-1,4-polyisoprene using Grubbs II as catalyst and DAB as CTA.

a broad range of new structures which were previously not accessible.

Highly involved in the development of polydiene chemistry, our group has focused its efforts on the development of one step telechelic polyisoprene synthesis from high molecular weight synthetic or natural polyisoprene either through an oxidative by oxidation [43–45] or metathetic methodologies [46,47].

In the present study, we first investigated a model polymer degradation reaction using Grubbs second generation catalyst to achieve the synthesis of low-molecular-weight acetoxy telechelic oligomers from synthetic polyisoprene (PI) and styrene–butadiene (SBR) copolymer. This degradation reaction was further extended to powders and granulates of waste tyres rubber to produce useful small molecules.

Polymer recycling is nowadays a subject of considerable importance, due to environmental, economic and social reasons. Many approaches have been used to extract value from waste materials, and can be divided into three broad categories: In the first approach, polymers can either be recycled chemically through degradation or depolymerization chemistry; in the second, they can be recycled physically through thermal reshaping into objects of lesser value than the original, but still useful in selected applications; in the last, waste polymers can simply be burned to extract their energetic value. Different chemical recycling processes have been examined for the recycling of waste tyres [48]. The novelty of recycling using metathesis lies in its ability to produce telechelic polymers from waste rubber, in one step under mild conditions [49]. The aim of the present study was to obtain raw materials from waste and their reuse for novel applications. In the present work, we specifically paid attention to the recycling of waste tyres.

Table 1
Metathetic degradation of cis-1,4-polyisoprene in toluene using cis-1,4-diacetoxy-2-butene as chain transfer agent and Grubbs II as catalyst. $t = 2$ h, [PI] = 0.36 mol L^{-1}, PI/CTA = 80.

Entry	PI/Grubbs II	$\overline{M}_n$ SEC (g mol^{-1})	$\overline{M}_w$ SEC (g mol^{-1})	PDI	Yield %
PI		222,000	446,000	2	
1	200	33,700	64,500	1.91	95
2	380	50,300	160,440	3.19	100
3	500	73,000	212,600	2.91	96
4	750	103,000	188,910	1.83	100
5	1000	93,000	213,000	2.29	98

Experimental average molecular weight measured by size exclusion chromatography (SEC) calibrated with polystyrene standards. PDI: polydispersity index measured by SEC.

Table 2
Metathetic degradation of cis-1,4-polyisoprene in toluene using cis-1,4-diacetoxy-2-butene as a chain transfer agent and Grubbs II as a catalyst. $t = 2$ h, PI/CTA = 80.

Entry	[PI] (moles/L)	PI/Grubbs II	$\overline{M}_n$ SEC (g mol^{-1})	$\overline{M}_w$ SEC (g mol^{-1})	PDI	Yield %
PI			222,000	446,000	2	
1	0.36	200	33,700	64,500	1.91	95
2	0.36	380	50,300	160,440	3.19	100
6	0.54	200	15,500	21,000	1.46	94
7	0.54	380	18,500	30,000	1.61	95

Experimental average molecular weight measured by size exclusion chromatography (SEC) calibrated with polystyrene standards. PDI: polydispersity index measured by SEC.

2. Experimental part

2.1. Materials

Cis-1,4-polyisoprene high-molecular weight ($\overline{M}_n$ = 222,000 g/mol) and styrene–butadiene rubber ($\overline{M}_n$ = 201,000 g/mol) were purchased from Acros Organics and purified prior to use. The cis-but-2-ene-1,4-diol (Aldrich) was distilled over $CaSO_4$ under a vacuum before any chemical modification. Cis-1,4-diacetoxy-2-butene (DAB) was synthesized according to the literature [50]. Tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] benzylidine ruthenium (IV) dichloride (second generation Grubbs catalyst), triethylamine, acetic anhydride, dichloromethane and methanol were purchased from Aldrich. Dichloromethane was first dried over calcium hydride overnight, and further distilled over phosphorus pentoxide. Other solvents were of reagent grade and used without any further purification. Waste tyre materials were kindly delivered from Delta Gom and their characterization was published in previous work [51].

2.2. Techniques

^1H spectra were recorded on a Bruker 400 Fourier transform spectrometer at 400.13 and 100.62 MHz, respectively in $CDCl_3$ with tetramethylsilane (TMS) as internal standard.

IR spectra were recorded on a Perkin–Elmer 1750 Fourier transform spectrometer in the 4000–500 cm^{-1} range.

The number-average molecular weight ($\overline{M}_n$) and molecular weight distribution (PDI) were measured by size exclusion chromatography (SEC). The SEC analysis was performed at 35 °C in THF (1.0 mL/min) as eluent, on a ThermoFinnigan SEC instrument (equipped with a SpectraSYSTEM injector), a pre-column (Polymer Laboratories, PL gel 5 μm Guard, 50 × 7.5) followed by 2 columns

Table 3
Metathetic degradation of cis-1,4-polyisoprene in dichloromethane using cis-1,4-diacetoxy-2-butene as chain transfer agent and Grubbs II as catalyst. [PI] = 0.01 mol L^{-1}.

Entry	Time of reaction (h)	PI/Grubbs II	PI/CTA	$\overline{M}_n$ SEC (g mol^{-1})	$\overline{M}_w$ SEC (g mol^{-1})	PDI	Yield %
PI				222,000	446,000	2	90
8a	4	200	200	900	1600	1.81	
8b	24	200	200	350	750	2.19	
9a	2	500	500	20,500	33,500	1.95	75
9b	4	500	500	10,300	16,900	1.66	
9c	24	500	500	5600	10,750	1.42	
10a	2	1000	1000	50,100	98,000	1.63	80
10b	4	1000	1000	17,200	28,700	1.6	
10c	24	1000	1000	7000	10,000	1.9	

Experimental average molecular weight measured by size exclusion chromatography (SEC) calibrated with polystyrene standards. PDI: polydispersity index measured by SEC.