ELSEVIER

Polymer 41 (2000) 827–830

polymer

The effect of vinylsilane on metathetical degradation and functionalization of 1,4-polybutadiene catalyzed by ruthenium carbene complexes

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Received 15 March 1999; received in revised form 31 March 1999; accepted 8 April 1999

Abstract

Polybutadiene (**I**) containing 91% 1,4-(*cis*/*trans*) units and 9% of 1,2 units, in the presence of vinyltriethoxysilane and ruthenium catalysts $Cl_2(PCy_3)_2Ru=CHPh$ (**II**) and $[RuCl_2(p\text{-cymene})]_2/N_2CHSiMe_3/PCy_3$ (**III**) at 60°C and at room temperature undergoes partial degradation and functionalization. At a ratio [vinylsilane]/[total $>C=C<$ of (**I**)] = 0.1, the reaction leads to a limited (compared to ethylene as a substrate) degradation and metathetical conversion of 1,4-polybutadiene (particularly *cis*-CH=CH units) with vinylsilane yielding silylated unsaturated oligomers. At a ratio [vinylsilane]/[total $>C=C<$ of (**I**)] = 1, a cross-metathesis of 1,2 $>C=C<$ groups of (**I**) with vinylsilane predominated over the degradation/cross-metathesis of 1,4-polybutadiene.

Keywords: 1,4-Polybutadiene; Metathetical degradation; Vinylsilane

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1. Introduction

Cross-metathesis of unsaturated polymers with alkenes (ethylene, octene, or styrene) occurs in the presence of classical Mo and W catalysts leading to oligomer[1–5] formation. Such a degradation of polymers to low-molecular weight products via olefin metathesis has been applied by Hummel et al. [3,4] for the study of cross-linked structures. In a similar way, silicon-containing olefins, mainly allylsilanes, were employed by Marmo and Wagener in metathetical degradation of 1,4-polybutadiene in the presence of a Schrock catalyst to yield perfectly difunctional ($f = 2.0$) telechelic polybutadiene oligomers [6,7]. Vinylsubstituted silanes, however, appeared to be inactive both for degradation of unsaturated polymers as well as for their ADMET polymerization in the presence of Mo- and W- carbene catalysts [8, 9].

Nevertheless, vinylsilanes were used for the reduction of the molecular mass of polymers [10]. Very recently vinyl–substituted silsesquioxane and spherosilicates have been reported to undergo cross–metathesis with alkenes in the presence of Schrock type catalyst– $[Mo(=CHCMe_2Ph)(NC_6H_3i\text{–}Pr_2\text{–}2,6)(OCMe(CF_3)_2)_2]$ [11]. The aim of this article is to report the use of vinylsilanes for degradation of 1,4-polybutadiene in the presence of ruthenium–carbene catalysts.

2. Experimental

2.1. Materials

Polybutadiene ($M_n = 400\ 000$) (**I**) containing 91% 1,4-(*cis*/*trans*) units and 9% of 1,2 units, was purchased from Polysciences Inc and used without additional purification. Vinyltriethoxysilane, purchased from Fluka A.G. was distilled prior to use. $Cl_2(PCy_3)_2Ru=CHPh$ (**II**) was purchased from Strem Chemicals and $[RuCl_2(p\text{-cymene})]_2$ was prepared by standard procedure [12]. This catalyst was activated by trimethylsilyldiazomethane from Aldrich (the ratio Ru: diazocompound = 1:4) in situ when added to the reaction mixture to form Ru = carbene [12].

2.2. Reactions

Reactions were carried out under argon, in a glass reactor equipped with a condenser and a heater or in sealed glass ampoules. In a typical reaction 1.00 g (0.001 mol) 1,4-polybutadiene, 24 g chlorobenzene, 0.16 cm^3 (or 1.60 cm^3) of vinyltriethoxysilane and 7.4×10^{-6} mol of catalyst were placed in the reaction system and heated for 24 h at 60°C.

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PII: S0032-3861(99)00265-7

Table 1
Molecular weights of the 1,4-polybutadiene (**I**) after undergoing metathetical degradation with ethylene and vinyltriethoxysilane catalyzed by ruthenium carbenes (Reaction conditions: temperature 60°C, time 24 h, molar ratio catalyst/silane = 0.01 (for details see Section 2))

Catalyst	M_w (GPC)			
	No olefin	Ethylene	[Vinylsilane]/[total >C=C< of (I)]	
			0.1	1.0
$Cl_2(PCy_3)_2Ru{=}CHPh$	30 000 (3.93)[a]	4 300 (4.81)[a]	51 000 (4.21)[a]	210 000 (3.04)[a]
$[RuCl_2(p\text{-cymene})]_2/N_2CHSiMe_3/PCy_3)$	96 000	74 000	113 000	127 000

[a] M_w/M_n.

Reaction mixtures were analyzed by NMR and GPC techniques. Polymeric products were precipitated from the solution with methanol, filtered, washed with methanol and dried under vacuum. IR and NMR spectra of the isolated polymer were performed. Reactions with ethylene were conducted in a steel bomb (60°C, 24 h) using 15 atm of ethylene and at a 500/1 polybutadiene to catalyst molar ratio.

2.3. Equipment and analytical measurements

^1H and ^{13}C NMR spectra were recorded on a Varian XL300 spectrometer. Gel permeation chromatography (GPC) data were collected using a Gilson HPLC system with 2 mm × 250 mm × 10 mm, Jordi-Gel DVB Column; 500, 100 Å using polystyrene standards. IR spectra (film or KBr pellet) were recorded using a FT-Bruker JFS-113v instrument.

3. Results and discussion

Polybutadiene (**I**) was used to study its metathetical degradation and eventual functionalization using two ruthenium catalysts—namely, carbene Grubbs catalyst $Cl_2(PCy_3)_2Ru{=}CHPh$ (**II**) and a catalytic system based on $[RuCl_2(p\text{-cymene})]_2/N_2CHSiMe_3/PCy_3$ (**III**) at 60°C and at room temperature. Both ruthenium catalysts are well known to catalyse ROMP of unsaturated olefins, e.g. cyclooctene [12] and norbornene [12,13]. To follow the effect of vinyltrialkoxysilane on the process under study, the GPC technique was used to measure the degree of the degradation of (**I**). Two systems promoting degradation of (**I**) with ethylene and in its absence catalyzed by Ru catalysts (**II**) and (**III**) were compared and used for comparison with other olefins. All the products of the degradation underwent spectroscopic analysis by ^1H and ^{13}C NMR and FT-IR. The molecular weights of the polymer resulting from metathetical degradation in the presence of added olefins and two catalysts are compiled in Table 1.

The initial molecular weight of (**I**) is 400 000 (M_w/M_n = 1.37). It appears that both systems catalyze metathetical degradation with ethylene (especially Grubbs catalyst) or without the addition of any olefin, either. Examples of

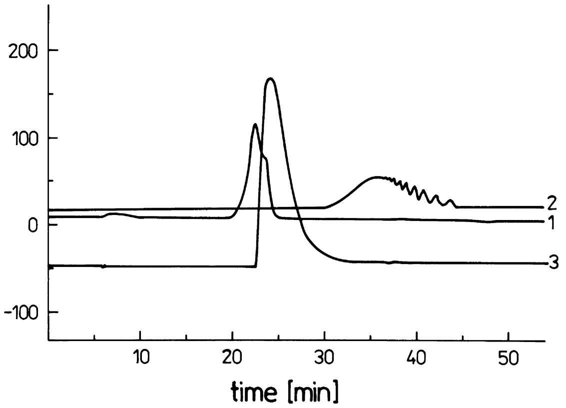

Fig. 1. GPC spectra of initial 1,4-polybutadiene (**I**) (1), and after undergoing degradation in the presence of catalyst (**II**); with ethylene (2) and vinyltriethoxysilane (3)-([vinylsilane]/[total >C=C< of (**I**)] = 0.1).

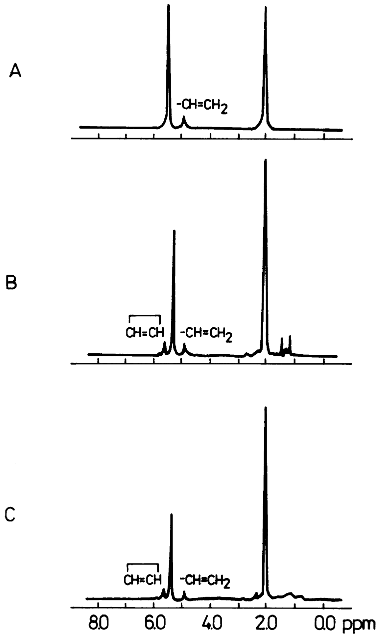

Fig. 2. ^1H NMR spectra of the initial 1,4-polybutadiene (A) and after undergoing catalytic degradation in the presence of catalyst (**II**) only-(B) and in the presence of ethylene and catalyst (**II**) (C).

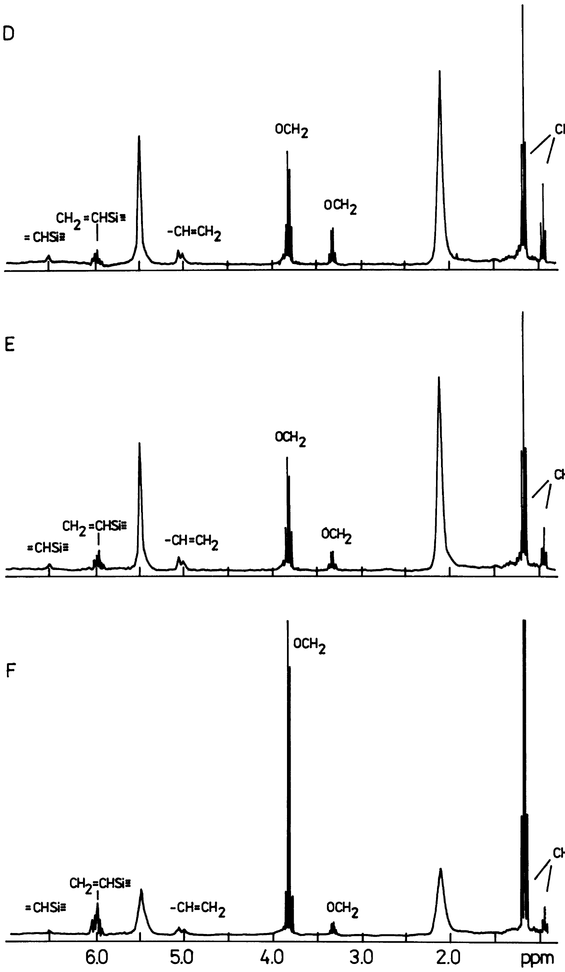

Fig. 3. ^{1}H NMR spectra of 1,4-polybutadiene after undergoing catalytic degradation/silylation with vinyltriethoxysilane in the presence of catalyst (**II**) (D, F) and catalyst (**III**)-(E) ([vinylsilane]/[total $>C=C<$ of (**I**)] = 0.1) (D, E) and 1 (F)).

GPC traces of (**I**), treated with ethylene and vinylsilane, are shown in Fig. 1.

The degradation took place to the same extent both at 60°C and at a room temperature with both catalysts used. The effect of vinylsilane is directly related to the ratio of the double bonds in (**I**) to vinylsilane. The effects of degradation are highlighted by the values of the molecular weights of the product after the reaction. Their decrease, with the increased concentration of vinylsilane used, is also worth emphasising. However, the key point is whether these lower M_W values result from lesser polymer degradation or a functionalization of the oligomers formed in the presence of vinylsilane.

The ^{1}H and ^{13}C NMR spectroscopy as well as IR study of degraded polymers were carried out to find evidence for functionalization, particularly in the presence of vinyltriethoxysilane.

Fig. 2 displays three ^{1}H NMR spectra (A–C), starting with that of the initial polymer (**I**) and isolated reaction products with catalyst (**II**) in the presence and in the absence of ethylene, respectively.

Fig. 3 presents the ^{1}H NMR spectra of reaction mixtures after 24 h heating (60°C) of (**I**) with vinyltriethoxysilane in the presence of a catalyst (**II**) (D and F) and (**III**) (E). ^{1}H as well as ^{13}C NMR spectra clearly indicate that functionalization (silylation) of the oligomers actually occurred in the course of cross–metathesis of vinylsilane with 1,4-polybutadiene. The ^{1}H NMR spectra of modified polymers (D–F) (Fig. 3) show resonances close to 6.00, 3.80 and 1.19 ppm, characteristic of the starting vinylsilane. Besides, new signals at 3.34 and 0.96 ppm can be attributed to ethoxy groups, which come from the silyl groups introduced to the chain and/or terminal and pendant $>C=C<$ groups of (**I**). Additionally, new $=CHSi\equiv$ resonances at 6.50 ppm could be found. ^{13}C NMR spectra, which show new carbon resonances attributed to carbon atoms of (OCH_2CH_3) substitutents of silyl groups, also support functionalization. The protons of the 9% of vinyl groups appear in the 4.95–5.01 ppm region. All the spectra (A–C) suggest that these groups remained unaffected, regardless of the procedure utilised (catalyst, temperature, ethylene added). Finally, new peaks observed in the ^{1}H NMR spectra in the 5.60–5.70 ppm region (Fig. 2(B) and (C)) are attributed to $CH=CH$ bonds of cyclic dienes and/or polyenes. This resonance has only been observed when (**I**) was reacted (in the presence of Ru carbene) with ethylene (Fig. 2(C)) and/or without any added olefin (Fig. 2(B)), confirming the idea of some extent of back-biting of polyenes during their degradation.

The observed ratio of internal $>C=C<$ to pendant $>C=C<$ in the treated (I) depends on the initial ratio of ([vinylsilane]/[total $>C=C<$ of (**I**)]). If the latter is approximately equimolar, a degradation/cross metathesis of the new vinyl groups in the chain of oligobutadiene is favoured (compared to reactivity of pendant $>C=C<$ groups (see Fig. 3(D) and (E). However, the tenfold excess of vinylsilane over the concentration of pendant $>C=C<$ groups (i.e. [vinylsilane]/[total $>C=C<$ of (**I**)] = 1, see Fig. 3(F)) leads to a decrease in the degradation process of (**I**), resulting in a lower functionalization of the vinyl groups in the chain and a more effective reaction of vinylsilane with pendant $>C=C<$ groups of (**I**).

The degradation/functionalization of 1,4-polybutadiene with vinylsilane was clearly confirmed by FT-IR spectroscopy results. The IR spectra (Fig. 4 (top)) of 1,4-polybutadiene (**I**) shows strong absorption at 965 and 911 cm^{-1}, characteristic of deformation vibrations of $=C–H$ bonds.

After the reaction of the initial polymer with vinyltriethoxysilane ([vinylsilane]/[total $>C=C<$ of (**I**)]) = 0.1), these two bands remain unchanged (Fig. 4, (bottom)). However, this spectrum reveals the presence of new bands at 1080 and 1105 cm^{-1}, attributable to Si–O–C vibration in ethoxysilyl groups, which also proves the occurrence of cross–metathesis of double carbon–carbon bonds of (**I**) with vinylsilane. It is also worth noticing that the band

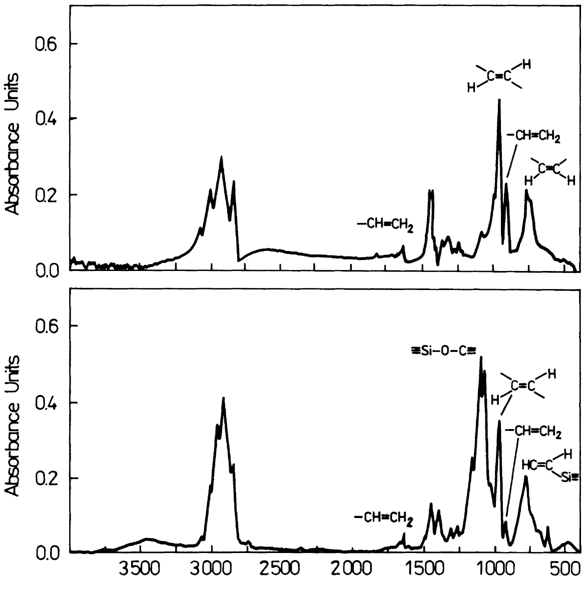

Fig. 4. FT-IR spectra of the initial (top) and silylated 1,4-polybutadiene (**I**) (bottom); ([vinylsilane]/[total >C=C < of (**I**)] = 0.1).

at 727 cm^{-1} (Fig. 4 (top)), presumably due to *cis*–HC=CH–deformation in the initial polymer (**I**) disappeared after cross–metathesis with vinylsilane. Simultaneously, the appearance of a new broad band at 776 cm^{-1} was observed. The latter can be considered as a characteristic deformation vibration of $-\text{CH}{=}\text{CHSi(OEt)}_3$ unit [14], i.e. the existence of real cross–metathesis of *cis*–CH=CH– bond of 1,4-polybutadiene with vinylsilanes. Such an effect can be supported by an earlier observation of cross–metathesis of polydodecenamer just with *cis*–1,4-polybutadiene—in the presence of a Calderon catalyst ($\text{WCl}_6/\text{EtOH}/\text{EtAlCl}_2$)[10]. Metathetical segment exchange between the two different polymers was taken as evidence for the formation of cis-1,4-polybutadiene units.

GPC, NMR as well as FT-IR spectroscopic studies allowed a description of the degradation process of 1,4-polybutadiene occurring in the presence of Ru carbenes. If the reaction takes place in the absence of any added olefin, the simple degradation scheme leads to a simultaneous formation of linear and cyclic oligomers. In the presence of ethylene, cross–metathesis with 1,4-polybutadiene proceeds, leaving the vinyl 1,2-units unaffected. This finally yields the most degraded oligomer (for Grubbs catalyst $M_w = 4300$), which also contains some cyclic units. Contrary to the self-metathetical transformation of (**I**), ring closure is observed after prior metathesis of 1,4-units by ethylene. In the presence of vinylsilane, cross-metathesis with (**I**) proceeds either via preliminary self-metathesis of (**I**) followed by cross–metathesis of the products with vinylsilane or, more probably, by direct metathetical conversion of 1,4-polybutadiene (particularly *cis*–CH=CH–units) with vinylsilane, yielding silylated unsaturated oligomers. Obviously, the reaction of (**I**) with vinylsilane (compared to ethylene as a substrate) leads to a more limited degradation of (**I**). This constitutes the first observation of polybutadiene functionalization via metathetical conversion with vinylsubstituted silanes.

Acknowledgements

Financial support by the State Committee for Scientific Research, Projects No 13T09 A 074 13 and No 3T09 B 023 12 is gratefully acknowledged.

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