APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 11, 843–849 (1997)

Catalysis of Hydrosilylation: Part XXXI.* Functionalization of Poly(methylhydro)siloxanes via Hydrosilylation of Allyl Derivatives

Bogdan Marciniec,[1]† Jacek Guliński,[1] Larysa Kopylova,[2] Hieronim Maciejewski,[1] Monika Grundwald-Wyspiańska[3] and Mariusz Lewandowski[1]
[1] Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland
[2] Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, 664033 Irkutsk, Russia
[3] Laboratory of Instrumental Analysis, Adam Mickiewicz University, 60-780 Poznań, Poland

The synthesis of functional poly(methylhydro)siloxanes has been successfully performed by effective quantitative hydrosilylation of allyl derivatives (allyl phenyl ether, allyl glycidyl ether, allyl methacrylate, allyl chloride, allylamine) and 1-octene with poly(methylhydro)siloxanes catalyzed by platinum [$Pt(PPh_3)_2(CH_2{=}CH_2)$, $PtCl_2(PPh_3)_2$, H_2PtCl_6–cyclohexanone] and ruthenium ($Ru_3(CO)_{12}$) complexes. The products were isolated and characterized by ^{1}H NMR, FT IR and GPC methods and can be regarded as examples of well-defined functionalized polysiloxanes with various practical applications. © 1997 John Wiley & Sons, Ltd.

Appl. Organometal. Chem. **11**, 843–849 (1997)
No. of Figures: 2 No. of Tables: 2 No. of Refs: 21

Keywords: catalysis; hydrosilylation; poly(methylhydro)siloxanes; allyl derivatives; platinum complexes; ruthenium complexes; functionalization of polymers

Received 10 March 1997; accepted 25 April 1997

INTRODUCTION

Polydimethylsiloxanes are characterized by a number of interesting properties, e.g. excellent heat resistance, low toxicity, biocompatibility, high oxygen permeability, poor wettability, extremely low surface tension, low melting point and glass transition temperature, resistance to radiation, special rheological properties, outstanding electrical isolating properties and others.[1] All the properties can be advantageously combined with other specific features of organic molecules and macromolecules introduced by covalent bond moieties into a non-polar matrix of silicones. Functional siloxanes find specific uses as elastomers, caulks, sealing agents, adhesives and release agents.[2]

Besides the process of equilibration, the hydrosilylation process[3] is the most widely used method of preparing organofunctional polydimethylsiloxanes[2, 3] starting from poly(methylhydro)siloxanes. Synthesis of hybrid materials of such a kind is usually performed directly by adding unsaturated derivatives of bulky molecules to a siloxane network (e.g. allyloxy end-blocked linear organic oligomers[4] to achieve a polymeric system miscible with organic polymers) as well as by adding macromolecules, e.g., carbohydrates, to poly(methylhydro)siloxanes to introduce hydrophilicity and chirality to the polysiloxane,[5] or by other methods directed to photo-crosslinkable and optically active side-chain liquid-crystalline copolymers.[6] These reactions frequently involve steric hindrances and, therefore, proceed only to a slight degree and lead to incomplete conversion of the Si–H groups.

Another method of chemical functionalization of polysiloxane chains involves preliminary introduction of side chains with terminal functional groups, e.g. ethers,[7–9] epoxy ethers[10–14]

---

* For part XXX, see B. Marciniec *et al.*, *J. Organomet. Chem.* **521**, 245 (1996).
† Correspondence to: Bogdan Marciniec.
Contract grant sponsor: Polish Committee for Scientific Research.

amines,[15] amides[16] and nitriles,[6] via usually smooth hydrosilylation of Si–H bonds with the corresponding allyl derivative.[3] Functional groups in side chains undergo further reactions. The subsequent reaction of the organofunctional groups with appropriate functional groups of organic macromolecules enables synthesis of many new amphilic polymers[5] or siloxane cationic surfactants.[10] The majority of functionalized siloxanes were designed to undergo thermally induced cross-linking, and to cure by hydrolytic processes or photochemically induced polymerization.[1]

Although numerous papers and patents have been devoted to the functionalization of poly(methylhydro)siloxanes via hydrosilylation (the functionality is fixed via Si–C groups), there is little quantitative and mechanistic information on the modification procedure, particularly on the efficiency of catalysts. The reaction has usually been reported to be catalysed by platinum complexes (mostly based on H_2PtCl_6 precursors).[4, 6, 7, 10, 11, 13, 14] Acidic Speier's catalyst could not be used for all the hydrosilylations since it causes isomerizations of the allylic bond, followed by acidic cleavage of the functional group[5] and, in some cases, gelation of the reaction mixture,[4] even during the process of addition. In such a case neutral Pt(0) and Pt(II) precursors are used; for example Pt/C,[10] $Pt_2[(CH_2{=}CH)SiMe_2OSiMe_2(CH{=}CH_2)]_3$,[9, 15] $PtCl_2(cod)_2$ (cod = cyclo-octadiene)[8] and $PtCl_2(C_5H_5)_2$.[5] Allyl derivatives with amido groups do not react with the Si–H bond of polysiloxanes in the presence of several platinum precursors but can be hydrosilylated in the presence of $[Rh_2Cl_2(cod)_2]$; however, this does not lead to quantitative conversion of Si–H.[16] Rh systems are applied occasionally.[16, 17]

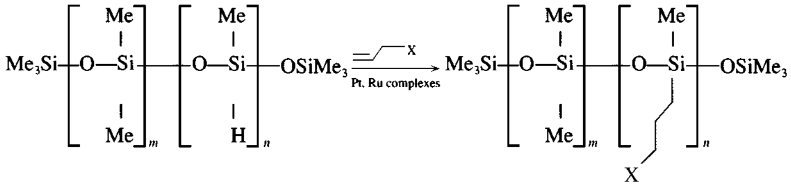
The aim of this paper is to find new effective catalysts (especially based on platinum and ruthenium precursors) for the reaction of poly(methylhydro)siloxanes with selected olefins, predominantly allyl derivatives, in order to devise a facile procedure for synthesis of polysiloxane coupling agents containing organofunctional groups in the side chain (in comparison to those with alkyl groups) as well as to characterize the modified poly(methylorgano)siloxanes prepared under the optimum conditions.

RESULTS AND DISCUSSION

Two model poly(methylhydro)siloxanes **A** and **B** were used to study the reaction of the Si–H bond with some allyl derivatives and 1-octene according to Scheme 1.

Pt(0)–$Pt(PPh_3)_2(CH_2{=}CH_2)$, Pt(II)–$PtCl_2(PPh_3)_2$ and H_2PtCl_6-based Pt(IV) (soluble in cyclohexanone) complexes, as well as $Ru_3(CO)_{12}$, were selected after preliminary tests as catalysts of this reaction. All of them were being used for the first time for modification of the polysiloxane chain. The Pt(0) complex was previously used successfully as a very effective catalyst for addition of trisubstituted silanes (trialkoxysilanes) to the C=C double bond of allyl derivatives as well as to alkenes.[18] $PtCl_2(PPh_3)_2$ is another example of Pt(II) chloride complexes used recently in hydrosilylation of allyl ethers.[8] Since Speier catalysts have been used frequently in most of the reactions being examined, another Pt(IV) complex was chosen so as to be able to compare the catalytic activity of Pt precursors. $Ru_3(CO)_{12}$ was recently used successfully in hydrosilylation of allyl chloride by trialkoxysilanes.[19] Selected catalytic results are compiled in Tables 1 and 2.

The conversion of poly(methylhydro)siloxane was studied using a quantitative IR method on the basis of absorption measurements at the Si–H stretching band frequency (max. 2167 cm^{-1}) with reference to the standard curve. It can be generally stated that under the optimum conditions (given catalyst, temperature and time of the



Scheme 1 Reaction of model poly(methylhydro)siloxanes **A** and **B** with allyl derivatives or 1-octene: $m=0$, $n=80$ (for **A**) or $m=21$, $n=42$ (for **B**); X = Cl, NH_2, CN, OPh, OCH_2—CH, $OC(O)C(CH_3){=}CH_2$ and $(CH_2)_4CH_3$.

Table 1 Effect of catalysts on the hydrosilylation of allyl derivatives and 1-octene with poly(methylhydro)siloxanes **A** and **B**

	Reaction conditions		SiH conversion (%)		
Allyl derivative	Temp. (°C)	Time (h)	$Pt(PPh_3)_2(CH_2{=}CH_2)$	H_2PtCl_6 (cyclohexanone)	$Ru_3(CO)_{12}$
$CH_2{=}CHCH_2Cl$	70	24	94	48	—
	70	48	96	63	—
	70	72	99	63	87
	90	6	94	61 (21)*	30 (18)*
	120	6	100	100 (57)*	100 (93)*
$CH_2{=}CHCH_2NH_2$	120	6	78	22	79
	140	3	90	96	79
$CH_2{=}CHCH_2CN$	120	6	10	14	28
	140	6	52	42	32
$CH_2{=}CH(CH_2)_5CH_3$	120	6	96	69	54

[a] Conditions: glass ampoules; [allyl derivative]:[siloxane]:[catalyst]$=1:1:5\times10^{-4}$; air; toluene as solvent.

[b] Results for substrate **B**.

reaction), functionalization of the poly(methylhydro)siloxane (type **A**) by the olefin used (except allyl cyanide) can proceed quantitatively. However, it is worth emphasizing that the $Pt(PPh_3)_2(CH_2{=}CH_2)$ complex is the most efficient catalyst, much more effective at lower temperature than Pt(IV) precursors in hydrosilylations of allyl chloride, allylamine and allyl phenyl ether as well as of 1-octene. On the other hand, the

Table 2 Effect of catalysts on the hydrosilylation of allyloxy derivatives with poly(methylhydro)siloxanes **A** and **B**[a]

	Reaction conditions		Si–H conversion (%)		
Allyl derivative	Temp. (°C)	Time (h)	**I/IV**[b]	**II**[b]	**III**[b]
$CH_2{=}CHCH_2OPh$	90	6	83/76	55 (27)[c]	50 (54)[c]
	120	6	98/99	99 (66)[c]	96 (88)[c]
	20	48	n.r.[d]	7	27
	20	72	n.r.	10	60
$CH_2{=}CHCH_2OC(O)C(CH_3){=}CH_2$	20	120	n.r.	12	93
	120	6	Polymer	80	Polymer
	20	24	n.r./71	82	33
	20	48	n.r./79	89	37
$CH_2{=}CHCH_2OCH_2\underline{CHCH_2O}$	20	72	n.r./86	93	40
	120	6	97/98	99	39

[a] Conditions: glass ampoules, [allyl derivative]:[siloxane]:[catalyst]$=1:1:5\times10^{-4}$; air, toluene as solvent.

[b] Catalysts: **I**, $Pt(PPh_3)_2(CH_2{=}CH_2)$; **II**, H_2PtCl_6 (cyclohexanone); **III**, $Ru_3(CO)_{12}$; **IV**, $PtCl_2(PPh_3)_2$.

[c] Results for substrate **B**.

[d] n.r., No reaction.

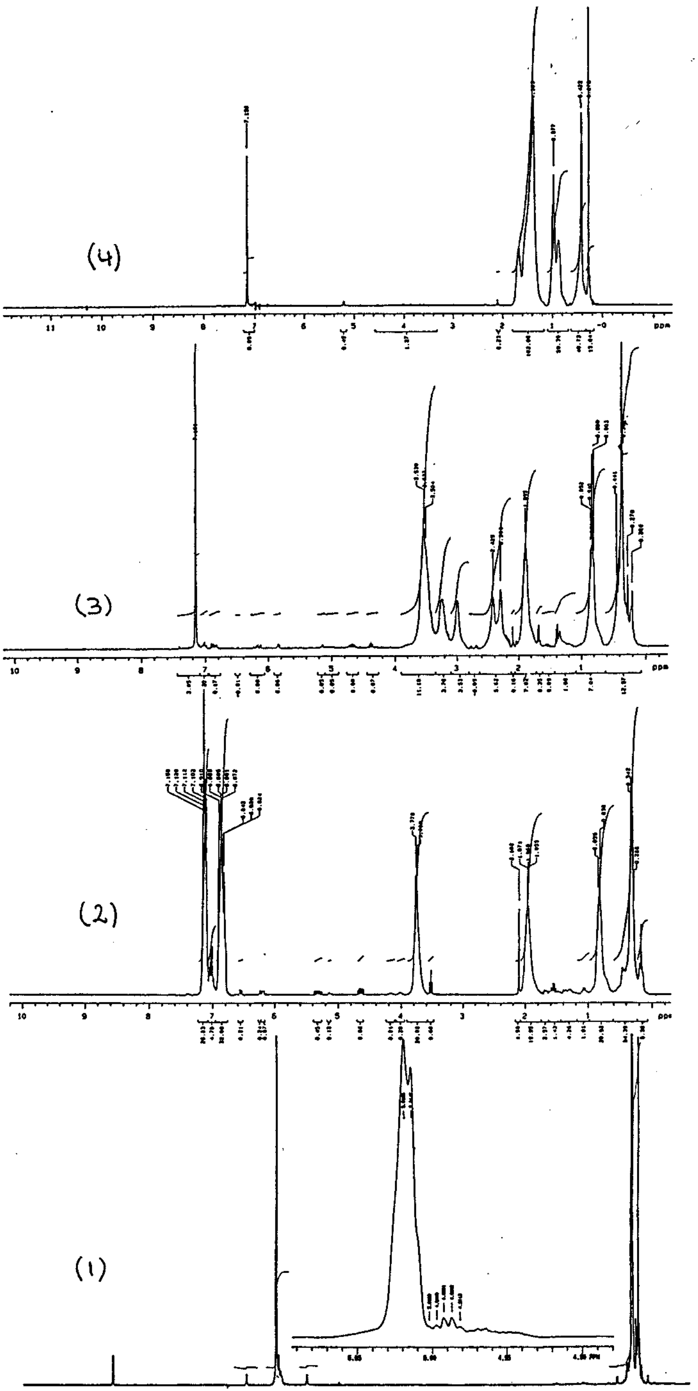


Figure 1 ^{1}H NMR spectra of poly(methylhydro)siloxane **A** (1), and of **A** modified with allyl phenyl ether (2), allyl glycidyl ether (3) or 1-octene (4) (for details see Experimental section).

H_2PtCl_6-based catalyst is a little more effective than the other platinum and ruthenium complexes in the hydrosilylation of allyl glycidyl ether, which confirms the previous data obtained with the use of the Speier catalyst.[11] The addition of allyl methacrylate to the Si–H bond of polysiloxane at elevated temperature is usually accompanied by vinyl polymerization (Table 2). Therefore, successful modification of polysiloxane by methacrylate as a result of hydrosilylation occurring in the presence of $Ru_3(CO)_{12}$ at room temperature seems to be a very practical method for synthesis of such polymeric coupling agents. The reaction of allyl phenyl ether with poly(methylhydro)siloxane **A** runs quantitatively at 120 °C in the presence of most catalysts used, but Ru(0) is more efficient than a H_2PtCl_6-based catalyst in the modification of polymethylhydrosiloxane **B**. The siloxane **A** was the subject of preparative reactions performed in the presence of a given catalyst and under conditions enabling almost quantitative yields from the hydrosilylation reactions (for details see the Experimental section). The products isolated from reactions of siloxane **A** with particular allyl derivatives and 1-octene were characterized mainly by ^{1}H NMR, FT IR and GPC methods.

Figure 1 presents ^{1}H NMR spectra of unmodified poly(methylhydro)siloxane **A** (1), and of **A** hydrosilylated with allyl phenyl ether (2), allyl glycidyl ether (3) or with 1-octene (4).

In all the isolated products, neither resonance of the Si–H (except for some traces) nor the respective allyl groups were noticed in the ^{1}H NMR spectrum. Appearance of new resonances, representative of the newly formed silylpropyl groups $\equiv SiCH_2CH_2CH_2Y$ (Y = functional group), indicated clearly the success of this functionalization of siloxanes. In the case of addition of allyl phenyl ether, besides CH_3Si signals, new ones derived from the $-CH_2CH_2CH_2O-$ chain (δ 0.95, 2.09, 3.88 ppm) and phenoxy group (δ 6.90–7.03 ppm) can easily be found in the resulting polymeric product. Similarly, for allyl glicydyl ether, characteristic signals attributed to the $-CH_2CH_2CH_2O-$ grouping were monitored (δ 0.96, 2.02, 3.65 ppm). Addition of 1-octene introduced an alkyl chain, $-CH_3(CH_2)_7-$, to the siloxane network (δ 0.54–1.50 ppm). Completion of all these reactions was confirmed by disappearance of the absorption band at 2167 cm^{-1} (ν_{Si-H}).

The resulting polysiloxanes modified by allyl glycidyl ether and allyl phenyl ether were subjected to GPC analysis (Fig. 2) to determine the scope of the modification of the siloxane **A**, i.e. to confirm quantitative introduction of the functional group to the polymer.

The chromatogram presented in Figure 2 shows unmodified polymer (1) and functionalized siloxanes (2, 3). The average molecular weight M_n = 4800 of the unmodified polysiloxane (degree of polymerization DP_n=80) increased after modification with allyl glycidyl ether (2) to M_n=13 800, i.e. confirming 100% reaction yield with the olefin. In the case of allyl phenyl ether (3), M_n=13 600 was observed, which corresponds to introduction of 82% of the propylphenoxy groups to the polysiloxane chain.

EXPERIMENTAL

Chemicals

Poly(methylhydro)siloxanes were purchased from Fluka (**A**, product A-938564) and General Electric (**B**, product SL 6020 D1) and were characterized by IR (KBr), ^{1}H NMR (C_6D_6) and GPC (THF) techniques.

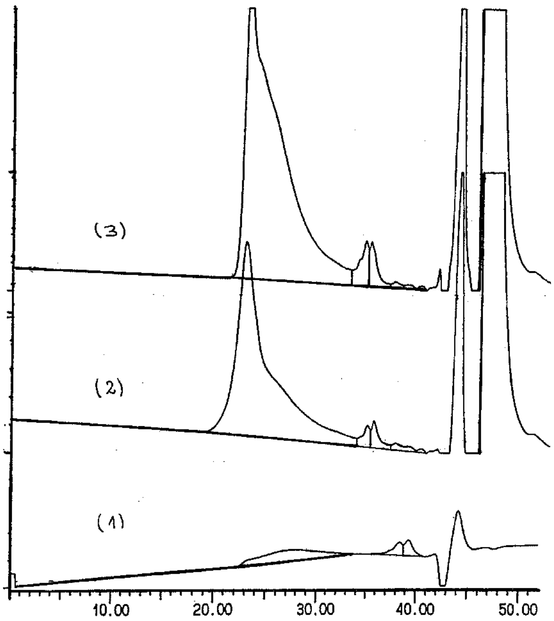


Figure 2 GPC spectra of poly(methylhydro)siloxane **A** (1), and of **A** modified with allyl glycidyl ether (2), and allyl phenyl ether (3) (for details see Experimental section).

A $\nu_{\text{Si–H}}$ 2167 cm^{-1}, $\nu_{\text{Si–O–Si}}$ 1098 cm^{-1}; $\delta_{\text{Si–H}}$ 5.12 ppm, δ_{CH_3} 0.34 ppm; M_n=4800, Dp$_n$=80
B $\nu_{\text{Si–H}}$ 2164 cm^{-1}, $\nu_{\text{Si–O–Si}}$ 1097 cm^{-1}; $\delta_{\text{Si–H}}$ 5.11 ppm, δ_{CH_3} 0.33 ppm; M_n=4300, Dp$_n$=62

All reagents were of at least laboratory grade. The following reagents were used as supplied from Fluka: 1-octene, allyl glycidyl ether, allyl chloride, allylamine, allyl cyanide, allyl phenyl ether and allyl methacrylate. $Pt(PPh_3)_2(CH_2{=}CH_2)$,[20] $PtCl_2(PPh_3)_2$[20] and H_2PtCl_6 in cyclohexanone[21] were prepared from $H_2PtCl_6 \cdot 6H_2O$ solution according to the literature indicated. $Ru_3(CO)_{12}$ was purchased from Strem Chemicals (now ABCR), Karlsruhe, Germany.

Typical procedure and product characterization

To a mixture of allyl derivative (2.5 mmol) and of poly(methylhydro)siloxane (**A** or **B**) (0.150 g) in toluene (2.5 ml), catalyst (10^{-3} mmol) was added. The reaction was allowed to proceed in sealed vials at the chosen temperature and reaction time. The reaction was judged to be complete by monitoring the disappearance of the Si–H absorption in the IR spectrum at 2167 cm^{-1}. The catalyst was removed via vacuum filtration, toluene was then removed *in vacuo* and the resulting polymers were isolated as clear oils. ^{1}H NMR, FT IR and GPC were used to characterize the products:

Functionalization with allyl glycidyl ether (120 °C, 7 h, $PtCl_2(PPh_3)_2$, glass ampoules, [allyl derivative]:[siloxane]:[catalyst] = 1:1:5 × 10^{-4}; air; toluene as solvent): ^{1}H NMR δ (ppm) 0.48 (CH_3Si), 0.96 ($CH_2CH_2C\underline{H}_2Si$), 2.02 ($CH_2C\underline{H}_2CH_2Si$), 2.48 ($OCH_2$), 3.25 (OCH), 3.65 ($C\underline{H}_2OCH$); GPC M_n=13 800.

Functionalization with allyl methacrylate (20 °C, 140 h, $Ru_3(CO)_{12}$, glass ampoules, [allyl derivative]:[siloxane]:[catalyst] = 1:1:5 × 10^{-4}; air; toluene as solvent): ^{1}H NMR δ (ppm) 0.48 (CH_3Si), 0.99 ($OCH_2CH_2C\underline{H}_2Si$), 1.75 ($CH_2{=}C(C\underline{H}_3)$), 2.04 ($OCH_2C\underline{H}_2CH_2Si$), 2.52 ($OC\underline{H}_2CH_2CH_2Si$), 5.74 ($C\underline{H}_2{=}C(CH_3)$; FT IR 1705 cm^{-1} (C=O).

Functionalization with allyl phenyl ether (120 °C, 6 h, $PtCl_2(PPh_3)_2$, glass ampoules, [allyl derivative]:[siloxane]:[catalyst] = 1:1:5 × 10^{-4}; air; toluene as solvent): ^{1}H NMR δ (ppm) 0.46 (CH_3Si), 0.95 ($OCH_2CH_2C\underline{H}_2Si$), 2.09 ($OCH_2C\underline{H}_2CH_2Si$), 3.88 ($OC\underline{H}_2CH_2CH_2Si$), 6.90–7.03 ($OC_6H_5$); FT IR (cm^{-1}) 1586 (aromatic >C=C<); GPC M_n=13 600.

Functionalization with allylamine (140 °C, 3.5 h, H_2PtCl_6 (cyclohexanone), glass ampoules, [allyl derivative]:[siloxane]:[catalyst] = 1:1:5 × 10^{-4}; air; toluene as solvent): ^{1}H NMR δ (ppm) 0.46 (CH_3Si), 1.0–3.45 ($CH_2CH_2CH_2NH_2$), 7.2–7.5 ($CH_2CH_2CH_2N\underline{H}_2$); FT IR (cm^{-1}) 3390, 3325 (N–H).

Functionalization with allyl chloride (120 °C, 6 h, $Ru_3(CO)_{12}$, glass ampoules, [allyl derivative]:[siloxane]:[catalyst] = 1:1:5 × 10^{-4}; air; toluene as solvent): ^{1}H NMR δ (ppm) 0.40 (CH_3Si), 0.98 ($ClCH_2CH_2C\underline{H}_2Si$), 1.48 ($ClCH_2C\underline{H}_2CH_2Si$), 3.30 ($ClC\underline{H}_2CH_2Si$).

Functionalization with 1-octene (120 °C, 6 h, $Pt(PPh_3)_2(CH_2{=}CH_2)$, glass ampoules, [allyl derivative]:[siloxane]:[catalyst] = 1:1:5 × 10^{-4}; air; toluene as solvent): ^{1}H NMR δ (ppm) 0.40 (CH_3Si), 0.54 ($CH_2CH_2C\underline{H}_2Si$), 1.10 ($CH_2C\underline{H}_2CH_2Si$), 1.50–1.60 ($(C\underline{H}_2)_n$.

Equipment and analytical measurements

GPC analyses

Gel-permeation chromatography (GPC) data were collected using a Gilson HPLC system with a 2 mm × 250 mm × 10 mm Jordi-Gel DVB column, 500, 100 Å. Relative number-average molecular weights of oligomers were determined by GPC using polysiloxane standards (analysis conditions: mobile phase THF; flow rate 0.75 ml min^{-1}; temperature ambient; injection volume 20 µl; detector RI (refractive index)).

FT IR analyses

The FT IR spectra were measured at 2 cm^{-1} resolution using a Bruker IFS 113v instrument, which was evacuated to avoid absorption of water and CO_2. Each spectrum consists of 250 scans at 31 °C in a cell with NaCl windows 0.1 mm thick.

^{1}H NMR analyses

The NMR spectra were recorded on a Varian XL 300 spectrometer. In all cases C_6D_6 was used as solvent.

CONCLUSIONS

CONCLUSIONS

Platinum [$Pt(PPh_3)_2(CH_2{=}CH_2)$, H_2PtCl_6 in cyclohexanone, $PtCl_2(PPh_3)_2$] and ruthenium [$Ru_3(CO)_{12}$] complexes appeared to be very effective catalysts for functionalization of poly(methylhydro)siloxanes by quantitative reaction with allyl derivatives such as allyl glycidyl ether, allyl phenyl ether, allylamine, allyl chloride and allyl methacrylate as well as with 1-octene. The functionalized polysiloxanes were isolated and characterized. The treatment of poly(methylhydro)siloxane does not change the average number of siloxane units and amendments to molecular weights are only due to the introduction of functional groups. These catalytic systems based on hydrosilylation can be extended to preparation of other reactive, well-defined, functionalized polysiloxanes which are of great practical importance as elastomers, caulks, sealing agents, adhesives and release agents.

Acknowledgement This work was supported by funds from the Polish Committee for Scientific Research, Research Project 7 S203 045 07 and 3 T09B 023 12.

REFERENCES

1. H. R. Kircheldorf (Ed.), *Silicon in Polymer Synthesis*, Springer, Berlin, 1996.
2. M. P. McGrath, E. D. Sall and S. J. Tremont, *Chem. Rev.* **95**, 381 (1995).
3. B. Marciniec (Ed.), *Comprehensive Handbook on Hydrosilylation*, Pergamon Press, Oxford, 1992.
4. T. Iwahara, M. Kusakabe, M. Chiba and K. Yonezawa, *J. Polym. Sci (A), Polym. Chem.* **31**, 2617 (1993).
5. G. Jonas and R. Stadler, *Acta Polym.* **45**, 14 (1994).
6. L. C. Chien and L. G. Cada, *Macromolecules* **27**, 3721 (1994).
7. G. Mao, F. Sun and D. W. Grainger, *Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.)* **34** (1), 134 (1993).
8. X. Cogueret and G. Wegner, *Organometallics* **10**, 3139 (1991).
9. Z. Zhu, A. G. Einset, Ch. Y. Yang, W. X. Chen and G. E. Wnek, *Macromolecules* **27**, 4076 (1994).
10. J. G. Matisons and A. Provatas, *Macromolecules* **27**, 3397 (1994).
11. X. Coqueret, A. Leblanche-Combier and C. Loucheux, *Eur. Polym. J.* **24**, 1137 (1988).
12. J. V. Crivello, B. Yang and W. G. Kim, *J. Polym. Sci (A), Polym. Chem.* **33**, 2415 (1995).
13. L. M. Khananashvili, D. A. Girgviliani, N. I. Tsomaya and T. N. Vardosanidze, *Int. J. Polym. Mater.* **28**, 43 (1995).
14. L. M. Khananashvili, D. A. Girgviliani, N. I. Tsomaya and T. N. Vardosanidze, *Synth. Prop. Polym.*, Vol. 55, Zaikov, G. E. (ed.), Nova Science, Cornneck, NY 1996, pp. 55–62; C. A. (1996), 350957.
15. H. Friedrich, I Jansen and K. Ruhlmann, *Polym. Degrad. Stab.* **42**, 127 (1993).
16. V. V. Braunmuhl, G. Jonas and R. Stadler, *Macromolecules* **28**, 17 (1995).
17. J. V. Crivello and M. Fan, *J. Polym. Sci., Polym. Chem. Ed.* **30**, 31 (1992).
18. B. Marciniec, J. Guliński, W. Urbaniak, T. Nowicka and J. Mirecki, *Appl. Organomet. Chem.* **4**, 27 (1990).
19. C. L. Schilling, European Patient 709 392 (1996).
20. V. V. Bashilov and V. I. Sokolov, *Izv . Acad. Nauk SSSR* 1188 (1986).
21. Polish Patent 144 753 (1984).