PII: S0032-3861(97)00034-7

Polymer Vol. 38 No. 20, pp. 5169–5172, 1997

0032-3861/97/$17.00 + 0.00

Functionalization of 1,2-polybutadiene by ruthenium complex catalysed coupling with vinylsilanes

Bogdan Marciniec*, Mariusz Lewandowski and Cezary Pietraszuk
Faculty of Chemistry, A. Mickiewicz University, 60-780 Poznań, Poland

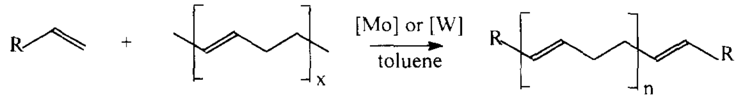
and Zenon Foltynowicz
Faculty of Commodity Science, Poznań University of Economics, 60-967 Poznań, Poland
(Received 29 July 1996; revised 4 January 1997)

Vinyl groups, i.e. 1,2-units of polybutadiene in the presence of various ruthenium complexes at elevated temperatures undergo an effective reaction of dehydrogenative coupling with vinyltrisubstituted silanes to yield silyl substituted units. This is a new type of functionalization of unsaturated polymers. The reaction products are identified by ^{1}H and ^{13}C n.m.r. and *FT*i.r. spectroscopies as well as g.p.c. methods. © 1997 Elsevier Science Ltd.

(Keywords: 1,2-polybutadiene; coupling; vinylsilane)

INTRODUCTION

Degradation of polymers with CH=CH bonds in the chain to low-molecular-weight products via olefin metathesis has been predominantly applied for the study of crosslinked structure[1,2]. Experimental procedure involves investigation of the degradation products by g.c.-m.s. method[3]. This method was applied to identify network structures in 1,4-polybutadiene after the reaction with dicumyl peroxide in solution[4]. Copolymers of 1,3-butadiene with styrene[5], propene[5], divinylbenzene/ethylvinylbenzene[7], acrylonitrile[8], vinyltrimethylsilane[2] and divinyldimethylsilane[1] have also been investigated. Cross-metathesis of unsaturated polymers with alkenes (mostly ethylene, octene) leading to oligomers, occurs in the presence of classical Mo and W catalysts[1–8]. Silyl olefins, mainly allylsilanes, were used by Wagener in ADMET depolymerization of 1,4-polybutadiene to yield—in the presence of well-defined Schrock catalyst—perfectly difunctional ($f = 2.0$) telechelic polybutadiene oligomers according to *Scheme 1*[9,10]:


where R = $CH_2Si(CH_3)_3$ or $CH_2Si(CH_3)_2Cl$; n = 1 - 4

Scheme 1

Crosslinking of the unsaturated polymers via metathetical conversion of hexenyl silicone polymers proceeding in the presence of Mo and W catalysts has been reported recently[11]. Vinylsubstituted silanes are not active in ADMET (de)polymerization in the presence of Mo and W catalyst[12,13], on the contrary, they can be used for the reduction of the molar mass of polymers[14].

On the other hand, divinylsubstituted silanes[15] and siloxanes[16] appeared very reactive in the new type of polycondensation reaction catalyzed by ruthenium and rhodium complexes, giving unsaturated polymers according to *Scheme 2*.

Recently, mechanistic evidence has been found (using monovinylsilanes) in support of the fact that the reaction occurs not via metathetical conversion (cleavage of the C=C bond), but via dehydrogenative silylation of olefins by vinylsilanes (i.e. cleavage of vinyl C–H in olefins and Si–C_{vinyl} bonds[17]). The same process proceeds in the cross-metathesis of vinylsilanes with olefins in the presence of many ruthenium complexes[18].

Therefore, the aim of this work is to utilize vinylsilanes not for depolymerization of 1,4- and 1,2-polybutadiene polymer to yield low-molecular oligomers, but for modification of polybutadiene to synthesize silylsubstituted polymers[19].

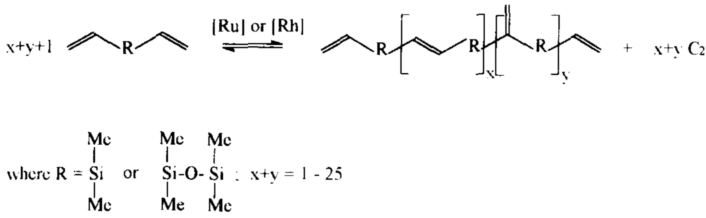
EXPERIMENTAL

Materials

1,2-Polybutadiene ($M_n = 1000$) and 1,4-polybutadiene ($M_n = 400\,000$) were purchased from Polysciences, Inc. and used without additional purification. Vinyltriethoxysilane

---

*To whom correspondence should be addressed



Scheme 2

and vinyltrimethylsilane were purchased from Fluka A.G. and were distilled prior to use. $Ru_3(CO)_{12}$, was purchased from Strem Chemicals and $[RuCl_2(CO)_3]_2$ was purchased from Aldrich Chem Co.; $RuCl_2(PPh_3)_3$, $RuHCl(CO)(PPh_3)_3$, $RuCl(SiMe_3)$ $(CO)(PPh_3)_2$ and $[RuCl_2(p\text{-cymene})]_2$ were prepared by standard procedures.

Reactions

Reactions were carried out in a glass reactor equipped with condenser and heater or in sealed glass ampoules. In a typical reaction 1.00 g (0.001 mol) 1,2-polybutadiene, 3.0 cm^3 toluene, 3.90 cm^3 (0.0185 mol) vinyltriethoxysilane (or 2.68 cm^3 (0.0185 mol) of vinyltrimethylsilane) and 1.85×10^{-4} mol of a catalyst were placed in the reaction system and heated for 24 h at 80°C. Polymeric products were precipitated from the solution with methanol, filtered, washed with methanol and dried under vacuum.

Equipment and analytical measurements

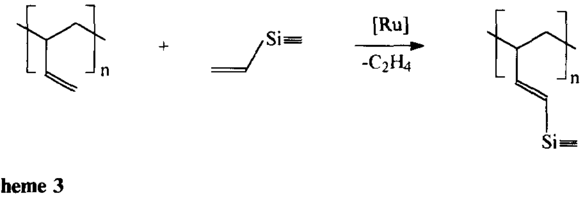
^{1}H and ^{13}C n.m.r. spectra were recorded on a Varian XL300 spectrometer. Gel permeation chromatography (g.p.c.) data were collected using a Gilson HPLC system with 2 × 250 × 10 mm, Jordi-Gel DVB Column; 500, 100 A using the polystyrene standards. I.r. spectra (film or KBr palette) were recorded using a FT-Bruker JFS-113v instrument.

RESULTS AND DISCUSSION

In our study two types of polybutadienes were used: 1,4-(*cis,trans*)-polybutadiene containing 9% of vinyl groups and 1,2-polybutadiene containing 85% of vinyl groups. The essential reaction of 1,2-polybutadiene with vinyltriethoxysilane and vinyltrimethylsilane proceeds according to *Scheme 3*.

As follows from the previously reported reactions of vinylsubstituted silanes with olefins the process is catalysed by many ruthenium complexes[20]. Exemplary catalytic data are compiled in *Table 1*. Conversion of vinyl groups in the polymer was followed by g.p.c. method (by comparing molecular weight of the initial and silylated polymers) and/or was calculated on the basis of ^{1}H n.m.r. spectra.

Figure 1 displays ^{1}H n.m.r. spectra of the initial (top) and silylated (bottom) 1,2-polybutadiene.



Scheme 3

Table 1 The effect of ruthenium catalyst on the conversion of vinyl groups and molecular weight (M_n) of the modified 1,2-polybutadiene

Catalyst	Conversion of vinyl groups (%)	M_n
$[RuCl_2(p\text{-cymene})]_2$	6.4	1080
$[RuCl_2(CO)_3]_2$	0.0	1000
$Ru_3(CO)_{12}$	0.0	1000
$Ru(SiMe_3)Cl(CO)(PPh_3)_2$	28.7	1360
$RuHCl(CO)(PPh_3)_3$	13.2	1160
$RuCl_2(PPh_3)_3$	60.3	1720

Reaction conditions: temperature: 80°C; time: 48 h; molar ratio catalyst/silane: 0.01; glass ampoules; M_n of the initial polymer = 1000

^{13}C n.m.r. and especially ^{1}H n.m.r. spectra are convincing evidence for real silylation of the polymer. As shown in ^{1}H n.m.r. (*Figure 1*) the modified polymer has a new proton resonance at the region 3.8 ppm and 1.1–1.6 ppm attributed to ethoxy substituents on silicon of the silyl group introduced to the chain. Moreover, the ^{1}H n.m.r. spectrum allows changes in the molecular weight of the silylated butadiene to be evaluated.

In the i.r. spectra (*Figure 2* top) of the initial 1,2-polybutadiene, a medium band at 1640 cm^{-1} due to stretching vibration of C=C of vinyl groups and a medium band at 3075 assigned to stretching vibrations of =C–H bond as well as a strong band at 909 and 968 cm^{-1} characteristic of deformation vibrations of =C–H bonds, were observed. After functionalizing of the polymer by its treatment with vinyltriethoxysilane, all these bands disappeared or markedly lowered (*Figure 2* bottom). Moreoever, the spectra reveal a presence of a new broad band at 1080 cm^{-1} attributable to Si–O–C vibration in the $CH{=}CHSi(OC_2H_5)_3$ groups which also proves functionalization of 1,2-polybutadiene. Simultaneously, a lowering of the bands at 723 cm^{-1}, which are due to *cis* –CH=CH– deformation vibrations (present in 1,2-butadiene in minor amounts) and appearance of a new broad band at 790 cm^{-1} were observed. The latter band presumably characterizes deformation vibration of $-CH{=}CH[Si(OEt)_3]$ unit. Activation of *cis* –HC=CH– to give $-CH{=}C[Si(OEt)_3]-$ cannot be excluded.

If the reaction of 1,2-polybutadiene with vinyltriethoxysilane is carried out at temperatures higher than 80–100°C, then, the dehydrogenative silylation of polymer is accompanied by crosslinking of the polymer.

The g.p.c. of the initial 1,2-polybutadiene (A) and treated with vinyltriethoxysilane at 80°C (B) and 120°C (C) is presented in *Figure 3*.

The molecular weight of the polymer (C) is 3200, while that of the polymer (B) is equal to 1700. Longer treatment of the polymer system at 120°C reveals an increase in its density and viscosity.

Silylation of 1,2-polybutadiene by vinyltrimethylsilane proceeds only at the temperature higher than 120°C and,

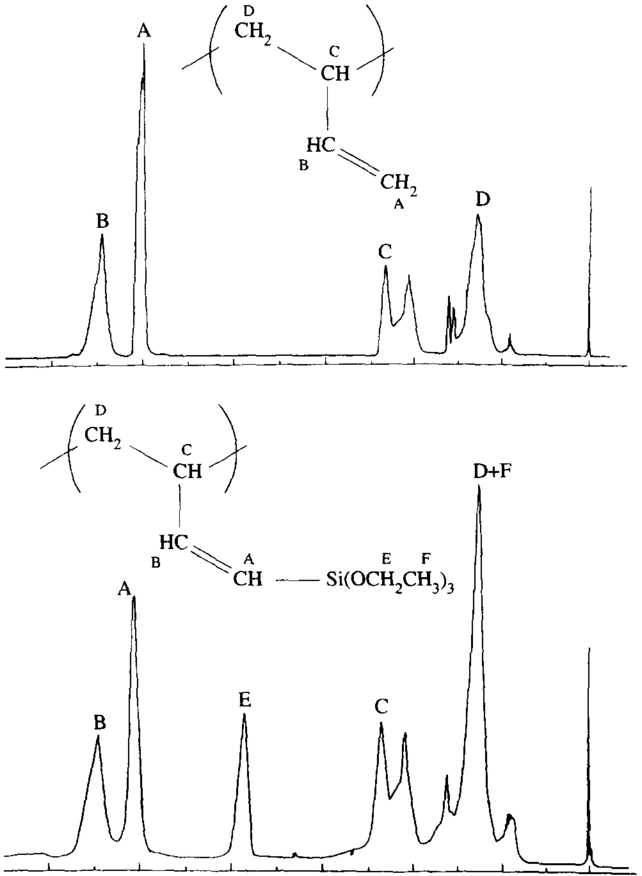


Figure 1 ^{1}H n.m.r. spectra of the initial (top) and silylated (bottom) 1,2-polybutadiene

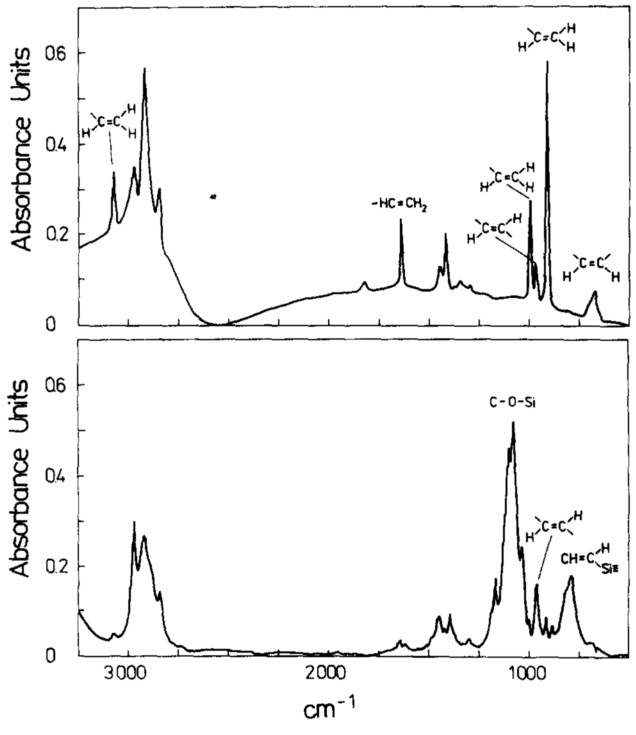


Figure 2 *FT*i.r. spectra of the initial (top) and silylated (bottom) 1,2-polybutadiene

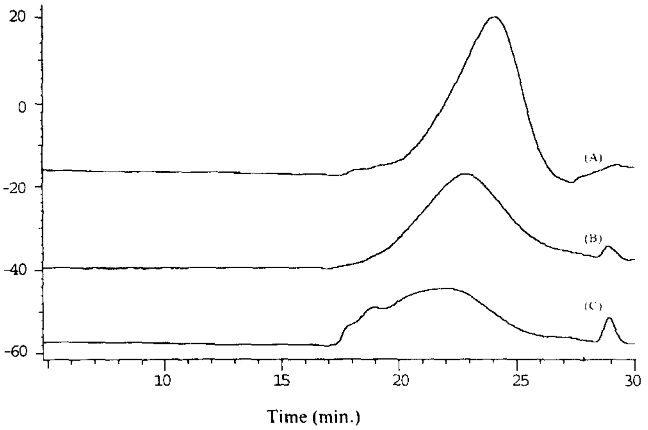


Figure 3 G.p.c. spectra of the initial 1,2-polybutadiene (A) and heated for 24 h with vinyltriethoxysilane at 80°C (B) and 120°C (C)

therefore, its products are always accompanied by the crosslinking phenomenon.

Similar series of the silylation of (*cis, trans*)-1,4-polybutadiene ($M_n = 400\,000$) by vinyltriethoxysilane was undertaken. The initial polybutadiene contained 9% of vinyl groups. Since in the i.r. spectra no band assigned for vinyl groups is observed after silylation, apparently, they all underwent reaction with vinylsilane in a similar way as in the case of 1,2-polybutadiene. Despite a lack of changes in the absorption band assigned to *trans* –HC=CH– vibrations in the 1,4-polybutadiene, the bands attributable to *cis* –HC=CH– deformation vibrations, and appearance of a new broad band at 788 cm^{-1}, characterizing deformation vibration of $-CH=C[Si(OEt)_3]$ and/or $-CH=CH[Si(OEt)_3]$ were observed. This can preliminarily be accounted for by activation of (*cis* –HC=CH) units in the dehydrogenative silylation of 1,4-polybutadiene by vinylsilanes under the conditions studied, but experiments are to be continued.

It can be concluded that facile functionalizing of vinyl groups in 1,2-polybutadiene by its coupling with vinylsilanes is a new type of modification of unsaturated polymers[19].

ACKNOWLEDGEMENT

This work was supported by funds from the State Committee of Scientific Research Project no. 7S 203 045 07.

REFERENCES

1. Hummel, K., Hubmann, E., Doesinger, M. and Pongratz, T., *Eur. Polym. J.*, 1991, **27,** 303.
2. Hubmann, E., Hummel, K., Doesinger, M., Pongratz, T. and Saaf, R., *Makromol. Chem.*, 1990, **191,** 1799.
3. Hummel, K., *J. Mol. Catal.*, 1985, **28,** 381.
4. Hummel, K., Chemelli, R., Grieber, H., Kumer, V.N.G. and Stelzer, F., *Makromol. Chem., Rapid Commun.*, 1983, **4,** 429.
5. Thorn-Csanyi, E., Abendroth, H. and Perner, H., *Makromol. Chem.*, 1990, **181,** 2081.
6. Hummel, K., Lechner, H., Zekoll, H. and Chemelli, R., *Makromol. Chem.*, 1987, **188,** 1075.
7. Hubmann, E., Loy, W.A., Th.Pngratz and Hummel, K., *Makromol. Chem.*, 1987, **188,** 2481.
8. Stelzer, F., Hobisch, G., Th.Pongratz and Hummel, K., *J. Mol. Cata.*, 1988, **46,** 433.
9. Marmo, J. C. and Wagener, K. B., *Macromolecules*, 1993, **26,** 2137.

10. Marmo, J. C. and Wagener, K. B., *Macromolecules*, 1995, **28**, 2602.
11. Stein, J., Lewis, L. N., Lettko, K. X. and Sumpter, C. A., *J. Inorg. Organometal. Polym.*, 1994, **4**, 367.
12. Smith, D. W. and Wagener, K. B., *Macromolecules*, 1993, **26**, 1633.
13. Finkelshtein, E. S. and Marciniec, B., in *Progress in Organosilicon Chemistry*, ed. B. Marciniec and J. Chojnowski. Gordon and Breach, 1995, p. 445.
14. Streck, R., *J. Mol. Catal.*, 1982, **15**, 3.
15. Marciniec, B. and Lewandowski, M. *J. Polym. Sci., Part A, Pol. Chem.*, 1996, **34**, 1443.
16. Marciniec B. and Lewandowski, M., *J. Inorg. Organometal. Polym.*, 1995, **5**, 153.
17. Marciniec B. and Pietraszuk, C., *J. Chem. Soc., Chem. Commun.*, 1995, 2003.
18. Marciniec, B., Pietraszuk, C. and Foltynowicz, Z., *J. Mol. Catal.*, 1992, **76**, 307.
19. McGrath, M. P., Sall, E. D. and Tremont, S. J., *Chem. Rev.*, 1995, **95**, 381.
20. Marciniec, B. and Gulinski, J., *J. Mol. Catal.*, 1984, **266**, C19.