A novel organometallic route to phenylethenyl-modified polysiloxanes

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Received 2nd September 2004, Accepted 1st November 2004
First published as an Advance Article on the web 19th November 2004
DOI: 10.1039/b413474e

We have synthesized a series of cyclic and linear siloxane materials with phenylethenyl substituents *via* transition metal complex-catalyzed coupling of the respective vinylsiloxane systems with styrene and α-methylstyrene. It has been shown that the non-carbene metal catalysts $[RuCl(H)(CO)(PPh_3)_3]$ and $[RuCl(SiMe_3)(CO)(PPh_3)_2]$ are the most effective ones, pointing to a silylative coupling pathway as the most plausible mechanistic route. The process was studied in the presence of a series of catalysts and styrene polymerization inhibitors under different reaction conditions, leading to useful silicone materials characterized by high refractive index values ranging from 1.51 to 1.59 due to strong π-conjugation in side chain substituents.

Introduction

In recent years there has been a growing demand for materials with properties which can not be provided by conventional polymers. Numerous specialty polymers can be utilized in such areas as interpenetrating polymer networks, thermally and chemically resistant materials, nonlinear optical materials, polymer liquid crystals and π-conjugated systems.[1–3] Within these, organometallic polymers are investigated extensively as their properties arise from both inorganic and organic components. Several authors have proven the utility of organosilicon polymers containing Si–O, Si–C and Si–N monomeric units, due to their thermal and optical behaviour.[4,5] For example, the syntheses of structurally diverse polymeric and oligomeric liquid crystal systems through new metal catalyzed metathesis or silylative coupling routes have been reported.[6–10]

There is an industrial demand for materials in personal care applications which have high refractive indices (RI), and silylative coupling routes offer the possibility of developing new materials or new methods to meet these needs. Aryl-substituted silicone fluids, typically made by hydrosilation of phenylacetylenes by Si–H substrates, are widely known as high RI materials.[11–13]

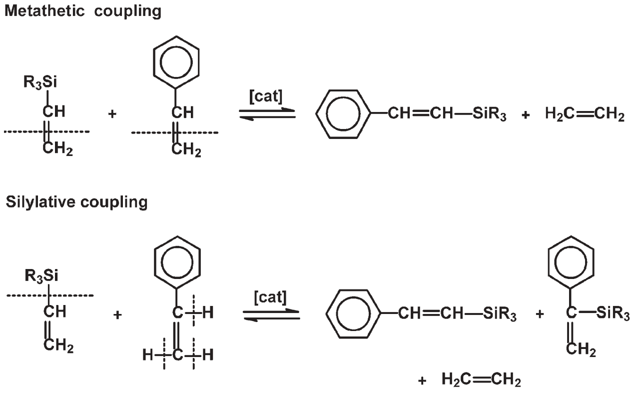
Clearly, both catalytic processes mentioned above can be developed into efficient synthetic methods for useful siloxane materials bearing phenylethenyl groups, which due to the electron conjugation impart high refractive indices. These processes could thus provide an alternative route to similar systems commonly prepared by hydrosilation. Both metathesis and silylative coupling lead to the same product, but of course differ mechanistically. Whereas metathesis involves C=C bond cleavage, silylative coupling occurs *via* =C–Si and =C–H bond breaking (Scheme 1), as shown in earlier work on simple deuterium labelled vinylsilanes.[14,15]

In this work, vinyl containing siloxanes, both linear (I) and cyclic (II) as well as diethoxysilane (III) (Scheme 2), were studied in coupling processes with styrene and α-methylstyrene, leading to fluids with high refractive indices. Such an approach provides a new modification route, alternative to hydrosilylation, for synthesis of phenylethenyl substituted siloxanes.

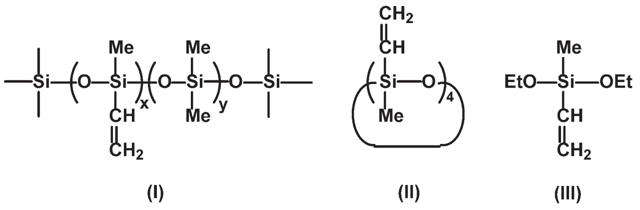
Experimental

Chemicals and procedures

Poly(dimethylsiloxane-*co*-methylvinylsiloxane)s were made from octamethylcyclotetrasiloxane (D_4, ABCR) and tetramethyltetravinylcyclotetrasiloxane ($D_4^{Me,Vi}$, ABCR) with hexamethyldisiloxane (MM, Aldrich) or octamethyltrisiloxane (MD_2M, GE) as chain terminating agents by ionic copolymerization (described below for a standard process).[16]



Scheme 1 Metathesis and silylative coupling routes.



Scheme 2 Vinyl containing siloxanes (I, II, III).

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α-Methylstyrene (Merck), styrene (Merck), toluene (POCh), hydroquinone (Aldrich), 4-*tert*-butylcatechol (Aldrich), 2,6-di-*tert*-butyl-4-methylphenol (BHT, Aldrich), $[RuCl_2(PPh_3)_3]$ (Aldrich), $[RuCl(H)(CO)PPh_3]$ (Aldrich), $[RuCl_2(=CHPh)(PCy_3)_2]$ (Strem) and $[\{(i\text{-}Pr)_2C_6H_3N=\}Mo(=CHCMe_2Ph)(biphen)]$ (biphen = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate, Strem) were used as supplied, whereas $[RuCl(SiMe_3)(CO)(PPh_3)_2]$[17] and $[Ru(OAc)H(CO)(PPh_3)_2]$[18] were prepared according to literature methods. Tris(hydroxymethyl)phosphine (Aldrich) was used to remove ruthenium complexes from final products.[19]

^1H, ^{13}C, and ^{29}Si (INEPT) NMR measurements were performed on either a Bruker AC 200 MHz or a Bruker DRX 500 MHz instrument. Size exclusion chromatography (SEC) was performed on a Wyatt Optilab 903 apparatus using two columns (TSK G4000HLX and G2000HLX) in a series with CH_2Cl_2 as the eluent. The instrument was calibrated using polystyrene standards. GC-MS analyses were run on a Thermo-Quest apparatus, while the spectra recorded by the MALDI-TOF technique were performed on a Voyager-Elite Perceptive Biosystems spectrometer.

Synthesis of poly(dimethylsiloxane-*co*-methylvinylsiloxane)s, representative procedure

A typical base catalyzed equilibration procedure was as follows: $D_4^{Vi,Me}$ (100 g, 1.16 mol of –SiMeViO– monomeric units), D_4 (43 g, 0.58 mol of $–SiMe_2O–$ monomeric units) and MD_2M (72 g, 0.232 mol) were stirred under nitrogen at 130 °C for 1 hour. At this time potassium silanolate (0.05 g, freshly made from octamethylcyclotetrasiloxane and KOH) was added, and the reaction mixture was stirred at 130 °C for 6 hours. It was then cooled to room temperature and neutralized with concentrated acetic acid to stop the equilibration. The resulting polymer was washed three times with MeOH (100 mL) and the volatile components were removed under vacuum (1 mmHg, 100 °C, 12 hours). Yield 155 g (72%); ^1H NMR ($CDCl_3$, ppm) δ: 0.09 (s, 6H, $–Me_2SiO–$), 0.16 (s, 3H, –*Me*ViSiO–), 5.73–6.11 (m, 3H, –Me*Vi*SiO–); ^{13}C NMR ($CDCl_3$, ppm) δ: −0.65 (–*Me*ViSiO–), 1.05 ($–Me_2SiO–$), 133.0 ($=CH_2$), 136.9 (=CH); ^{29}Si NMR ($CDCl_3$, $Cr(acac)_3$, ppm) δ: −0.34 (–MeViSiO–), −20.5 ($–Me_2SiO–$), 8.50 (Me_3Si end groups); SEC (THF) M_n = 1250, M_w/M_n = 1.3.

In the case of acid catalyzed processes, H_2SO_4 (0.6 mL) or CF_3COOH (0.15 mL) were used. Occasionally, D_3 served as a source of dimethylsiloxane monomeric units instead of D_4. Experimental details are summarized in Table 1.

Silylative coupling of copolysiloxane of average structure $[Me_3SiO(MeViSiO)_{53\%}(Me_2SiO)_{47\%}SiMe_3$; M_n = 1250] with styrene, representative procedure

Copolysiloxane (100 g, 0.66 mol of –[–SiMeViO–]– monomeric units), styrene (137.4 g, 151 mL, 1.32 mol), $[RuCl(H)(CO)(PPh_3)_3]$ (4.71 g, 0.005 mol) and an inhibitor (BHT, 0.29 g, 1.3· × 10^{-3} mol) were stirred under argon at 100 °C for 191 h. After that time the conversion, as measured by ^1H NMR spectroscopy, was 90%. The polymer was precipitated with MeOH (2 L) and then taken up in pentane, filtered and dried under vacuum for 4 days at room temperature. Styryl modified polysiloxane $Me_3SiO\text{-}[SiMe(CH=CH\text{–}Ph)O]_{48\%}[SiMeViO]_{4\%}[SiMe_2O]_{47\%}SiMe_3$ was obtained. Yield 115 g (77%); ^1H NMR ($CDCl_3$, ppm) δ: 0.05–0.25 (m, $–Me_2SiO–$), 0.25–0.45 (m, –MeSiO–), 6.25–6.60 (d of m, Si*CH*=CHPh, $J_{CH=CH}$ = 19.2 Hz), 6.95–7.25 (d of m, SiCH=*CH*Ph, $J_{CH=CH}$ = 19.2 Hz), 7.25–7.70 (m, Ph); ^{13}C NMR ($CDCl_3$, ppm) δ: (−0.05)–(0.03) (–*Me*SiO–), 0.09–1.65 ($–Me_2SiO–$), 1.70–2.25 (Me_3Si end groups), 125.5–126.5 (Si*CH*=CHPh), 126.6–128.5 (aromatic CH), 137.5–138.5 (aromatic C_q), 145–146 (SiCH=*CH*Ph); ^{29}Si NMR ($CDCl_3$, $Cr(acac)_3$, ppm) δ: (−34.5)–(−29.2) [SiMe(CH=CHPh)O] (in sequences of monomeric units), (−22.1)–(−17.9) ($SiMe_2O$ in sequences of monomeric units), 7.8–9.4 (Me_3SiO in sequences of monomeric units), SEC (THF): M_n = 1050; M_w/M_n = 1.6.

Silylative coupling of tetramethyltetravinylcyclotetrasiloxane ($D_4^{Vi,Me}$) with styrene, representative procedure

$D_4^{Vi,Me}$ (100 g, 1.36 mol [–SiMeViO–] molecular units), styrene (181.2 g, 1.74 mol), toluene (80 mL), $[RuCl(H)(CO)(PPh_3)_3]$ (5 g, 5.1 × 10^{-3} mol) and hydroquinone (0.83 g, 7.5 × 10^{-3} mol) were stirred under argon at 100 °C for 96 h. Then MeOH (300 mL) was added in order to precipitate polystyrene. The mixture was filtered and the volatile materials were removed under reduced pressure. The resulting oily, opaque, green residue was washed with 300 mL of MeOH, filtered and dried under vacuum again. The greenish product was dissolved in 300 mL of pentane and left in a refrigerator for 12 h. It was filtered cold and the pentane was evaporated. The transparent, brownish, oily residue was dissolved again in pentane, kept in a refrigerator for 3 h, filtered, evaporated and

Table 1 Equilibration process parameters

Molar ratio of organosilicon substrates									
$D_4^{Me,Vi}$	D_3	D_4	MM	MD_2M	Catalyst	M_n	M_w/M_n	–MeViSiO– m.u. (%)	Reaction time/h
1	—	0.50	0.10	—	H_2SO_4	4060	4.00	53	72
1	—	0.50	—	0.10	H_2SO_4	9450	3.95	52	96
1	3.40	—	0.20	—	H_2SO_4	3280	1.36	50	24
1	0.55	—	0.20	—	CF_3COOH	5000	1.29	67	240
1	—	0.50	—	0.15	$[KO(SiMe_2O)_xK]$	2670	1.12	56	7
1	—	0.50	—	0.20	$[KO(SiMe_2O)_xK]$	1740	1.13	65	7
1	—	0.50	—	0.10	$[KO(SiMe_2O)_xK]$	3200	1.10	65	7

[a] $D_4^{Me,Vi}$ – tetramethyltetravinylcyclotetrasiloxane, D_3 – hexamethylcyclotrisiloxane, D_4 – octamethylcyclotetrasiloxane, MM – hexamethyldisiloxane, MD_2M – decamethyltetrasiloxane. [b] Synthesis of poly(dimethylsiloxane-*co*-methylvinylsiloxane)s.

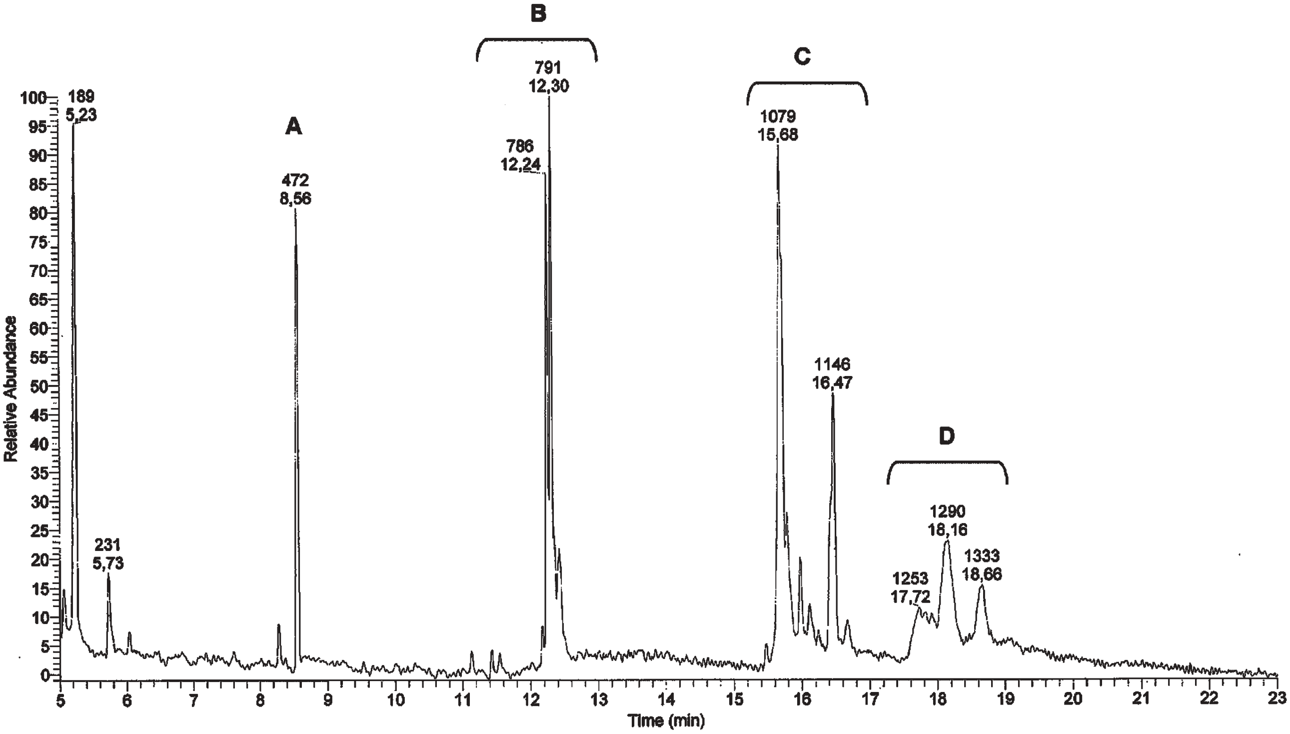


Fig. 1 GC/MS analysis of silylative coupling products of $D_4^{Vi,Me}$ and styrene.

dried under vacuum for 12 h, at 100 °C. Yield 104.5 g (43%). ^1H NMR ($CDCl_3$, ppm) δ: 0.12–0.15 (m, 3H, *Me*SiViO), 0.15–0.25 (m, 3H, *Me*SiCH=CHPh), 5.70–6.05 (m, 3H, unreacted Vi), 6.25–6.5 (m, 1H Si*CH*=CHPh, $J_{CH=CH}$ = 18.9 Hz), 6.90–7.1 (m, 1H, SiCH=*CH*Ph, $J_{CH=CH}$ = 18.9 Hz), 7.20–7.50 (m, Ph). ^{13}C NMR ($CDCl_3$, ppm) δ: (−1.1)–(−0.8) (–*Me*SiO–), 0.46–1.1 (–Me_2SiO–), 125.0–125.6 (Si*CH*=CHPh), 128.0–128.5 (aromatic CH), 133.5–135.7 (aromatic C_q), 145.3–148.7 (SiCH=*CH*Ph); ^{29}Si NMR ($CDCl_3$, $Cr(acac)_3$, ppm) δ: (−22.5)–(−20.7) [MeSi(CH=CHPh)O]– (in sequences of monomeric units).

Proportions of monomeric units (^1H NMR): 47% of –[MeSiCH=CHPhO]– and 53% of –[MeSiViO]–; SEC (CH_2Cl_2): M_n = 450, M_w/M_n = 1.24; EI GC/MS (Fig. 1) (*m*/*z*): **A** $[Si(Me)(Vi)O]_4$ (retention time 8.56 min) 329 (M^+ − Me, 60%), 317 (M^+ − Vi, 22%), 302 (M^+ − Me − Vi, 28%), 275 (M^+ − Me − 2Vi, 50%) ; **B** $[Si(Me)(Vi)O]_3[Si(Me)(CH{=}CHPh)O]$ (retention times 12.24, 12.30, 12.36 min) 420 (M^+, 1%), 405 (M^+ − Me, 5%), 317 (M^+ − CH=CHPh, 4%), 302 (M^+ − CH=CHPh − Me, 6%), 275 (M^+ − CH=CHPh − Me − Vi, 100%); **C** $[Si(Me)(Vi)O]_2[Si(Me)(CH{=}CHPh)O]_2$ (retention time 15.68 min) 496 (M^+, 10%), 481 (M^+ − Me, 2%), 393 (M^+ − CH=CHPh, 50%), 378 (M^+ − CH=CHPh − Me, 35%), 290 (M^+ − 2CH=CHPh, 50%), 275 (M^+ − Me − 2CH=CHPh, 72%); **D** $[Si(Me)(Vi)O][Si(Me)(CH{=}CHPh)O]_3$ (retention times 18.16, 18.66 min) 572 (M^+,1%), 366 (M^+ − 2CH=CHPh, 3%), 351 (M^+ − Me − 2CH=CHPh, 4%).

Silylative coupling of tetramethyltetravinylcyclotetrasiloxane $D_4^{Vi,Me}$ with α-methylstyrene, representative procedure

$D_4^{Vi,Me}$ (99.7 g, 0.34 mol) and α-methylstyrene (274 g, 2.32 mol) were stirred in toluene (100 mL) at 100 °C, in the presence of $[RuCl(H)(CO)(PPh_3)_3]$ (10.9 g, 0.011 mol). Progress of coupling was followed by ^1H NMR spectroscopy. The reaction was stopped after 96 h (52% conversion of vinyl groups). At this stage the reaction mixture was cooled to room temperature and 10 mL of MeOH was added in order to deactivate the catalyst. The solvent was evaporated leaving a green oily liquid. This liquid was dissolved in pentane (200 mL) and then left in a refrigerator overnight, filtered and evaporated giving 105 g of the cyclic siloxanes. Yield 179.7 g (69%). ^1H NMR ($CDCl_3$, ppm) δ: 0.12–0.15 (m, 3H, *Me*SiViO), 0.15–0.25 (m, 3H, *Me*SiCH=C(Me)Ph), 2.18 (s, 3H, MeSiCH=C(*Me*)Ph), 5.80–6.10 (m, 3H, unreacted Vi), 6.45–6.60 (m, 1H, Si*CH*=), 7.30–7.55 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, ppm) δ: (−0.8)–(−0.4) (–*Me*SiO–), 1.1–1.3 (–Me_2SiO–), 18.4–18.9 (MeSiCH=C(*Me*)Ph), 128.7–129.8 (aromatic CH), 133.4–136.0 (aromatic C_q), 148.5–149.3 (SiCH=*CH*Ph). ^{29}Si NMR ($CDCl_3$, $Cr(acac)_3$, ppm) δ: (−23.5)–(−22.4) [SiMe(CH=CMePh)O] (in sequences of monomeric units).

Proportions of monomeric units (^1H NMR): 52% of –{MeSi[CH=C(Me)Ph]O}– and 48% of –[MeSiViO]–; SEC (CH_2Cl_2): M_n = 500, M_w/M_n = 1.28.

$MeViSi(OEt)_2$

Two methods were used. (**A**): A THF solution of EtONa was prepared by allowing sodium metal (12.5 g, 0.54 mol) to react with ethanol (43.2 g, 0.94 mol) in THF (160 mL). The reaction was carried out at room temperature for 20 h. Then $MeViSiCl_2$ was added dropwise to the solution, and the reaction mixture was stirred for 4 h. The solution was diluted with pentane (300 mL) and washed with ice water. The organic layer (pH = 7) was separated and dried over $MgSO_4$. The solvent was evaporated and the product was distilled at reduced pressure to give 12.6 g (34%) of $MeViSi(OEt)_2$. B.p. 40 °C at 20 mmHg (lit.:[20] 133–134 °C/760 mmHg). ^1H NMR ($CDCl_3$, ppm) δ: 0.15 (s, 3H, Me); 1.18 (t, 3H, OCH_2CH_3, J_{H-H} = 7.0 Hz); 3.47 (q, 2H, OCH_2CH_3, J_{H-H} = 7.0 Hz); 5.97 (m, 3H, $CH{=}CH_2$); ^{13}C NMR ($CDCl_3$, ppm) δ: −4.78 (Me); 18.23 (OCH_2CH_3), 58.19 (OCH_2CH_3), 133.72 ($CH{=}CH_2$), 135.01 ($CH{=}CH_2$); ^{29}Si NMR ($CDCl_3$, $Cr(acac)_3$, ppm) δ: −18.6; GC-MS (EI): 159 ($M^+ - H$, 10%), 145 ($M^+ - Me$, 100%), 115 (28%), 101 (36%), 89 (37%), 61 (34%), 45 (42%).

(B): A mixture of EtOH (200 mL, 3.42 mol) and pyridine (277 mL, 3.43 mol) was added dropwise to a stirred solution of $Cl_2SiMeVi$ (211 mL, 1.62 mol) in dry pentane (1200 mL). The temperature was kept in the range of 15–20 °C. After the addition was completed, the reaction mixture was stirred for 4 hours at room temperature and left overnight. Then, pyridine hydrochloride was filtered off, the solution was concentrated and distilled (133 °C at 760 mmHg) to give $MeViSi(OEt)_2$. Yield 114.5 g (65%).

$Me(EtO)_2SiCH{=}CHPh$

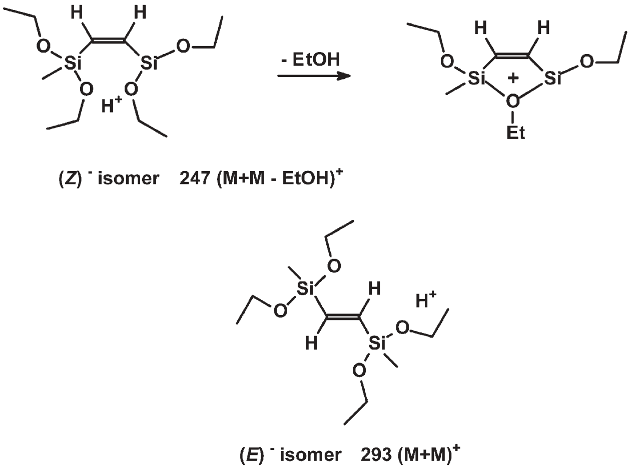
$Me(EtO)_2SiVi$ (150 mL, 0.8 mol) and styrene (370 mL, 3.23 mol) were stirred in the presence of $[RuCl(H)(CO)(PPh_3)_3]$ (4.66 g, 4.9 mmol) at 100 °C for 190 h. The reaction was monitored by GLC. Polystyrene (182 g, no inhibitor was used) was precipitated in pentane and the cross-coupled product $[Me(EtO)_2SiCH{=}CHPh]$ was purified by distillation (60 °C at 0.2 mmHg) giving 163.5 g (86%). ^1H NMR ($CDCl_3$, ppm) δ: 0.32 (s, 3H, Me), 1.29 (t, 3H, CH_2CH_3, J_{CH-CH} = 7.1 Hz), 3.86 (q, 2H, CH_2CH_3, J_{CH-CH} = 7.1 Hz), 6.35 (d, 1H, Si–CH=, $J_{CH=CH}$ = 19.3), 7.15 (d, 1H, =CHPh, $J_{CH=CH}$ = 19.3), 7.25–7.50 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$, ppm) δ: −4.58 (Me), 17.84 (CH_2CH_3), 57.82 (CH_2CH_3), 122.03 (SiCH=), 126.29–128.14 (CH, Ph), 137.37 (C_q, Ph); 147.00 (=CHPh); ^{29}Si NMR ($CDCl_3$, $Cr(acac)_3$, ppm) δ: −17.6; MS (EI): 236 (M^+, 10%), 221% ($M^+ - Me$, 60%), 177 (50%), 147 (85%), 131 (100%), 117 (50%), 105 (45%), 77 (75%), 61 (50%), 45 (70%).

Side products of the homocoupling of $Me(EtO)_2SiCH{=}CH_2$ (∼10%) were *Z* and *E* stereoisomers of $Me(EtO)_2SiCH{=}CHSi(OEt)_2Me$ in a ratio 2 : 1 (GC) as determined by GC/MS analyses of the reaction mixture. In EI ionization mode, both isomers showed the same fragmentation pattern with $M^+ - Me$ at 277. The two isomers could be differentiated by CI (isobutene), since they gave different principal peaks *viz.* $Me(EtO)_2SiCH{=}CHSi(OEt)_2Me$ (*Z*): 247 (M + H − EtOH) and $Me(EtO)_2CH{=}CH(OEt)_2Me$ (*E*): 293 (M + H) (Scheme 3).

Co-hydrolysis of $Me(EtO)_2SiCH{=}CHPh$ with $Me_2Si(OEt)_2$

$Me(EtO)_2SiCH{=}CHPh$ (96.6 g, 0.41 mol), $(EtO)_2SiMe_2$ (26.64 g, 0.18 mol), Me_3SiCl (23.8 g, 0.22 mol) and water (78 mL, 4.33 mol) were stirred in diethyl ether (250 mL) for 100 h at room temperature. The organic phase was separated, washed with water until pH 7 was achieved and dried over $MgSO_4$. The solvent was evaporated yielding 96 g (97%) of a pale yellow viscous liquid.

^1H NMR ($CDCl_3$, ppm) δ: 0.2–0.6 (m, MeSi resonances for sequences of monomeric units), 6.4–6.6 (m, SiCH=CHPh resonances for sequences of monomeric units), 7.1–7.3 (m, SiCH=CHPh resonances for sequences of monomeric units), 7.35–7.7 (m, Ph); ^{13}C NMR ($CDCl_3$, ppm) δ: (−0.4)–(0.2) (–*Me*ViSiO–), (0.08)–(1.3) ($–Me_2SiO–$), (1.7)–(2.0) (Me_3Si end groups), (125.0)–(126.0) (Si*CH*=CHPh), (126.6)–(128.5) (aromatic CH), (138.0)–(138.5) (aromatic C_q), (145.5)–(146.5) (SiCH=*CH*Ph); ^{29}Si NMR ($CDCl_3$, $Cr(acac)_3$, ppm) δ: (−33.2)–(−30.6) ([SiMe(CH=CHPh)O] in sequences of monomeric units), (−23.1)–(−17.8) ($SiMe_2O$ in sequences of monomeric units), 7.6–8.7 (Me_3SiO in sequences of monomeric units) (Fig. 2).



Scheme 3 *Z* and *E* isomers of $Me(EtO)_2SiCH{=}CHSi(OEt)_2Me$.

Results and discussion

The functionalization of silicones was studied focusing on the coupling of styrene and α-methylstyrene with both linear (I) and cyclic siloxanes (II) (Scheme 2). The corresponding monomer, diethoxy(methyl)(phenylethenyl)silane, was also made by the same route in order to check the efficiency of the synthetic approach in a more straightforward manner (Scheme 4).

High refractive index optical fluid applications require that the viscosity of the material be limited,[21,22] thus the highest value of M_n of the starting linear siloxanes used was ∼3200 daltons. However, conditions of acid and base catalysed equilibration of tetramethyltetravinylcyclotetrasiloxane ($D_4^{Me,Vi}$) with hexamethylcyclotrisiloxane (D_3) or octamethylcyclotetrasiloxane (D_4), in the presence of end blockers such as hexamethyldisiloxane (MM) or decamethyltetrasiloxane (MD_2M), can be adjusted to give linear products of various chain lengths (see Experimental section and Table 1).

Initial experiments performed with ruthenium and molybdenum complexes (Table 2) allowed for a comparative evaluation of catalytic activity of the respective organometallic compounds. Additionally, they also provided an opportunity to evaluate the likelihood or effectiveness of the two possible mechanistic pathways leading to the final phenylethenyl substituted siloxanes (using catalysts known to promote either metathetical or silylative coupling). Considering the final material, from the practical point of view it did not matter, of course, which of the two processes prevailed as in both couplings the desired copolymers bearing variable amounts of

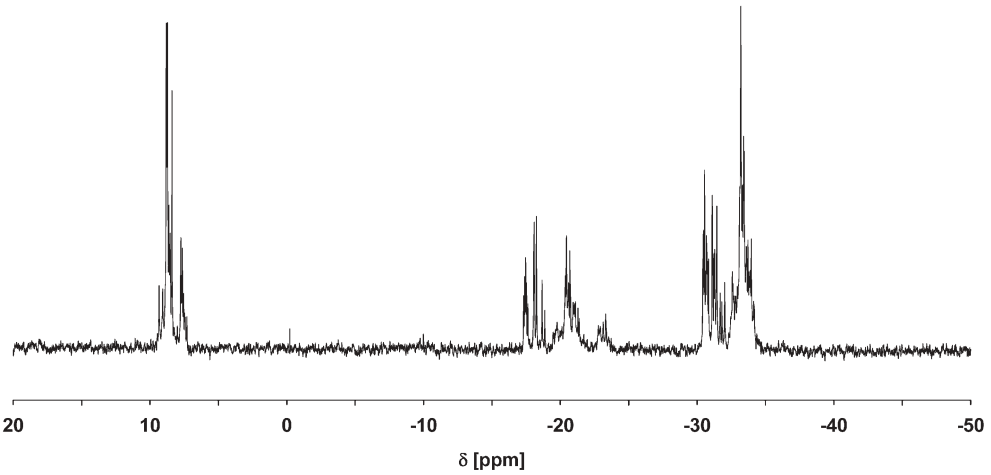
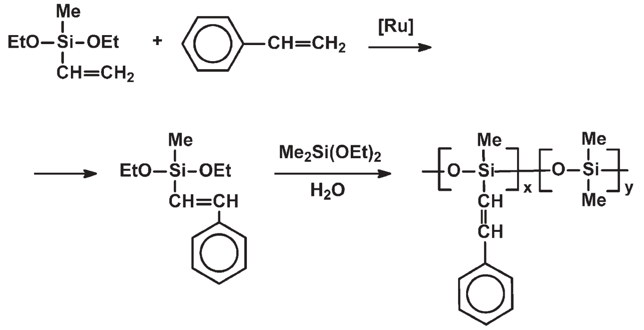


Fig. 2 ^{1}H NMR spectrum of co-hydrolysis product of $Me(EtO)_2SiCH{=}CHPh$ and $Me_2Si(OEt)_2$.

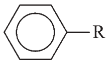


Scheme 4 Synthesis of phenylethenyl-modified siloxanes—an alternative route.

phenylethenyl groups are being formed. However, it was important to understand the effect of key variables such as the type of catalyst, catalyst concentration, styrene concentration and type of solvent present on the course of the reaction, as well as the extent of polystyrene production. Polystyrene is often formed in this type of reaction as a byproduct *via*, presumably, free radical polymerization (strong EPR signals were reported, for example, in reaction systems containing $[RuCl_2(PCy_3)_2({=}CHPh)]^{23}$).

Results obtained for the coupling of linear polymethylvinylsiloxane (M_n = 3200, IP = 1.1) with styrene (Table 2) show the effects of process variables and type of catalyst on the progress of the reaction. The first six entries refer to the use of the metallacarbene complexes benzylidene-bis(tricyclohexylphosphine)dichlororuthenium and 2,6-diisopropylphenylimidoneophylidene-(racemic BIPHEN)-molybdenum, for reactions run in both CH_2Cl_2 and toluene. In each case, a very small extent of coupling (*via* metathesis) was observed together with a large amount of polystyrene, even in the presence of hydroquinone as a free radical quencher.

Table 2 Coupling of linear poly(dimethylsiloxane-*co*-methylvinylsiloxane) (65% of –MeViSiO– m.u., M_n = 3200) with styrenes

	 —R	Catalyst[a] (%wt)	Inhibitor[b] (%wt)	Styrene molar excess per –MeViSiO– m.u. (%)	T/°C	Solvent	Reaction time/h	Coupling (%)	Molar content of PS[b] (%)
1	$–CH{=}CH_2$	I (2)	—	50	40	CH_2Cl_2	6	45	45
2	″	I (2)	—	50	40	CH_2Cl_2	6	8	18[c]
3	″	I (2)	—	50	100	toluene	48	28	35
4	″	I (2)	QUIN (0.2)	100	100	toluene	12	20	28
5	″	II (1.5)	—	100	100	toluene	48	gel formation	—
6	″	II (1.5)	—	100	40	CH_2Cl_2	96	36	7
7	″	III (2)	—	50	110	n-decane	48	58	19
8	″	III (2)	—	50	110	PhCl	72	36	25
9	″	III (2)	CAT (0.5)	100	100	toluene	48	30	1
10	″	III (2)	CAT (0.5)	50	100	toluene	144	72	0
11	″	III (2)	BHT (0.5)	100	100	toluene	92	86	0
12	″	III (2)	QUIN (0.5)	100	100	toluene	102	100	0
13	″	IV (2)	QUIN (0.5)	100	100	toluene	20	0	38
14	″	V (2)	BHT (0.5)	100	100	toluene	92	95	0
15	$–C(CH_3){=}CH_2$	III (2)	—	100	100	toluene	96	70	—
16	$–CH{=}CH_2$	VI (1)	—	100	100	toluene	93	0	—

[a] I – (Grubbs catalyst) benzylidene-bis(tricyclohexylphosphine)dichlororuthenium; II – (Schrock's catalyst) 2,6-diisopropylphenylimidonephenylidene-(racemic BIPHEN)molybdenum, III – $RuCl(H)(CO)(PPh_3)_3$; IV – $Ru(OAc)H(CO)PPh_3)_2$; V – $RuCl(SiMe_3)(CO)(PPh_3)_2$, VI – $RuCl_2(PPh_3)_3$. [b] QUIN – hydroquinone; CAT – 4-*tert*-butylcatechol; BHT – 2,6-di-*tert*-butyl-4-methylphenyl; PS – polystyrene. [c] Drop-wise addition of styrene (5 h).

Among ruthenium complexes reported to promote silylative coupling, the effectiveness increased in the following order: $[RuCl_2(PPh_3)_3] \sim [Ru(OAc)(H)(CO)(PPh_3)_2] \ll [RuCl(H)(CO)(PPh_3)_3] \sim [RuCl(SiMe_3)(CO)(PPh_3)_2]$. Although the catalytic efficiencies of $[RuCl(H)(CO)(PPh_3)_3]$ and $[RuCl(SiMe_3)(CO)(PPh_3)_2]$ were comparable, the latter was much less stable, so further experiments with other silicon substrates were carried out in the presence of $[RuCl(H)(CO)(PPh_3)_3]$.

Our observations seem contrary, in two aspects, to previous reports concerning analogous processes with simple, non-polymeric vinylsilanes. First, successful coupling between vinyltriethoxysilane and styrene was reported in the presence of $[RuCl_2(PPh_3)_3]$.[24] $[Ru(OAc)(H)(CO)(PPh_3)_2]$ was also found to be effective in silylative coupling polycondensation of dimethyl(*p*-vinylphenyl)vinylsilane.[25] In our work, both complexes turned out to be inactive as silylative coupling catalysts. Moreover, in all reactions, where styrene was one of the substrates, significant amounts of polystyrene were always found. To our surprise this has not been reported earlier.[14] Importantly, formation of large amounts of polystyrene can be avoided by the use of free radical quenchers such as hydroquinone, 4-*tert*-butylcatechol or 2,6-di-*tert*-butyl-4-methylphenol (entries 9–14, Table 2), except in the case of $[Ru(OAc)(H)(CO)(PPh_3)_3]$, which, as mentioned, was totally ineffective in catalyzing the silylative cross coupling reaction under the studied conditions. The optimum conditions found for the linear polymethylvinylsiloxane functionalization included 100% molar excess of styrene, a level which raises the importance of adding a radical quencher to the reaction. The only other way of avoiding formation of the polyolefin as a side product is to perform the cross coupling of polymethylvinylsiloxane with α-methylstyrene. With α-methylstyrene, the equilibrium between monomer and polymer favors the monomer under typical reaction conditions due to steric hindrance. However, the relevant coupling yield was lower than in the case of unsubstituted styrene (entry 15, Table 2). The same picture is valid for silylative coupling of tetramethyltetravinylcyclotetrasiloxane with styrenes (Table 3), *i.e.* the yields are lower for α-methylstyrene (entries 1–4) compared to those with unsubstituted styrene (entries 5–8).

Although no homopolymerization occurred in the case of α-methylstyrene coupling even in the absence of added inhibitor(s), it was found that the addition of BHT, hydroquinone or 4-*tert*-butylcatechol led to an increase in the coupling yield (*e.g.* ~20% in the presence of BHT). In reactions involving styrene and the cyclic siloxane, polystyrene was formed even in the presence of each of the three inhibitors. However, the homopolymer was easily removed from the mixture of phenylethenylated cyclosiloxanes upon the addition of methanol and subsequent filtration.

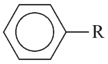
In experiments with cyclic silicone substrate, 100% conversion was not reached, and conversions were lower with α-methylstyrene than with styrene. Byproducts included a mixture of cyclic derivatives from which the desired product could be isolated by chromatography. It was found, in reactions in which inhibitor was used, that the coupling yield could be improved under certain reaction conditions (see, for example, entry 6 in Table 3, where 90% conversion was obtained). The coupling products of $D_4^{Me,Vi}$ and styrenes were mono-, di-, tri-, and presumably tetra-substituted cyclic siloxanes. The latter could not be resolved by GC under the conditions used. In the case of monophenylethenyl derivatives, three isomers are evident in the GC/MS spectra (Fig. 1, retention times 12.24, 12.30 and 12.35 min). They were assumed to be *Z* and *E* isomers containing –[PhCH=CHSi(Me)O]– monomeric units as well as a product of styrene coupling *via* α-C–H bond cleavage, leading to α-phenylethenyl-substituted cyclosiloxane with a $[CH_2=C(Ph)–]$ side group.

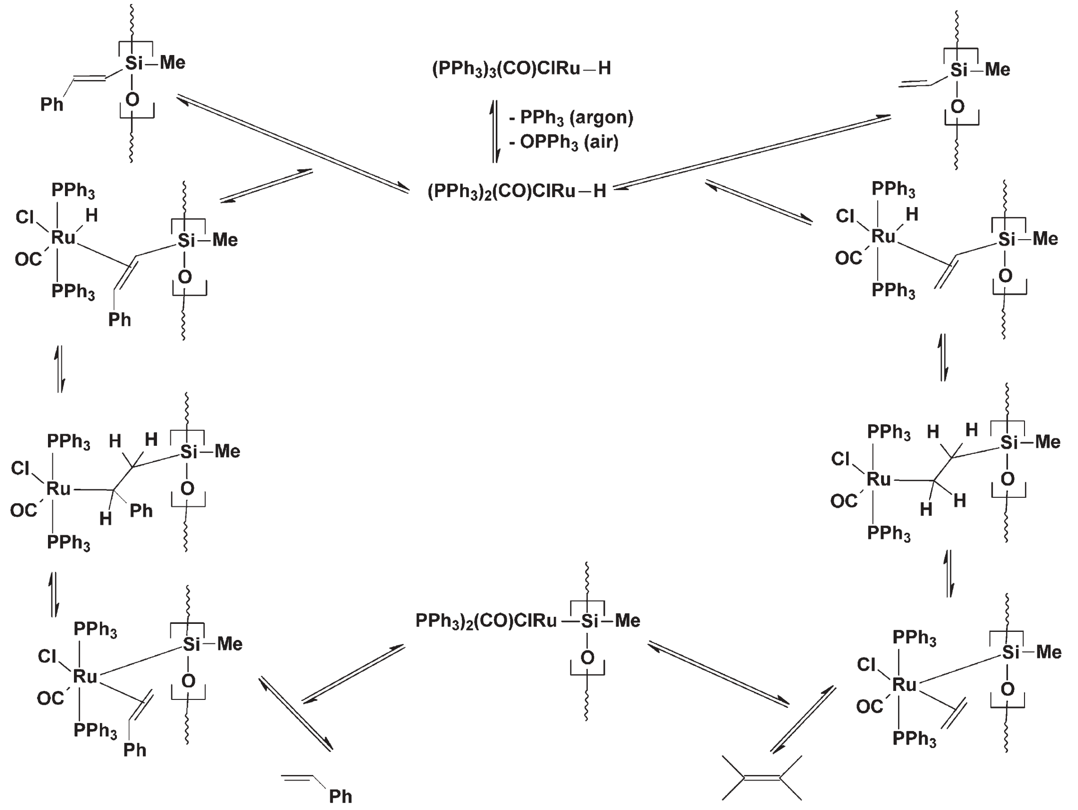
The presence of the third isomer as well as low effectiveness of metallacarbene type catalysts (Table 2) point clearly to the silylative coupling process as an efficient pathway in reactions of vinylsiloxanes with styrenes. Although no kinetic data were collected for these reactions, as mechanistic studies were not the primary objective of this work, it seems justified to adapt the mechanism suggested first by Wakatsuki *et al.*[26] for coupling of low molecular species catalysed by ruthenium complexes (Scheme 5).

Higher substituted cyclosiloxanes can be seen as broadened signals in the range of 15.68–16.47 min and 17.72–18.66 min in the GC plot shown in Fig. 1. Their respective EI MS spectra correspond to di- and tri-substituted cyclosiloxanes. In all cases, unreacted tetramethyltetravinylcyclotetrasiloxane appears as well (not marked on GC plot) having a retention time of ~8.50 min. These results suggest that under such reaction conditions, only silylative coupling occurred. Linear polymers resulting from ring-opening processes were not detected.

An alternative synthesis of phenylethenylsiloxanes involved a sort of reverse sequence of reactions (Scheme 4). The difunctional monomer methylvinyldichlorosilane was ethoxylated to

Table 3 Coupling of $D_4^{Me,Vi}$ with styrenes {$[RuCl(H)(CO)(PPh_3)_3]$, 100 °C, toluene}

		$RuCl(H)(CO)(PPh_3)_3$ (%wt)	Inhibitor (%wt)	Styrene molar excess per –MeViSiO– m.u. (%)	Reaction time/h	Coupling (%)	Molar content of PS (%)
1	$–C(CH_3)=CH_2$	1.50	—	100	96	39	0
2	″	1.50	BHT (0.3)	100	96	47	0
3	″	1.50	BHT (0.3)	100	120	61	0
4	″	1.50	CAT (0.3)	100	48	31	0
5	$–CH=CH_2$	1.50	QUIN (0.1)	50	96	63	17
6	″	1.50	QUIN (0.5)	100	48	90	18
7	″	0.44	QUIN (0.3)	100	96	68	21
8	″	1.50	CAT (0.5)	100	96	46	9



Scheme 5 Mechanism of silylative coupling in the presence of ruthenium complex.

give the corresponding diethoxy derivative. Subsequent silylative coupling of this monomer with styrene yielded $Me(EtO)_2SiCH{=}CHPh$, a suitable source of phenylethenyl containing monomeric units for hydrolytic polycondensation reactions. The ethoxylation reaction gave higher yields when carried out with ethanol in the presence of pyridine as the HCl acceptor. Silylative coupling with styrene, in the presence of $[RuCl(H)(CO)(PPh_3)_3]$ (Table 4), gave three products. They were the (*E*) and (*Z*) isomers of $Me(EtO)_2SiCH{=}CHSi(OEt)_2Me$, formed in a relatively small amount as a result of homo-coupling of vinylsilane, and the expected cross-coupling product $Me(EtO)_2SiCH{=}CHPh$ (*E*). Use of the alternative catalyst $[RuCl(SiMe_3)(CO)(PPh_3)_2]$ led to a higher amount of homo-coupled products, however when the reaction was carried out with large excess of styrene (as a reactant and diluent), 99% of methyl(phenylethenyl)diethoxysilane was obtained. The small amount of isomeric substituted ethenes were separated from the desired product by distillation, because in the subsequent hydrolytic condensation reaction their presence could lead to highly cross-linked siloxane products. Attempts to obtain the corresponding α-methylstyryl derivative by the same route failed. The only products, independent of the type of ruthenium catalyst used, were the two isomers of methylvinyldiethoxysilane resulting from homocoupling.

Hydrolysis of methyl(phenylethenyl)diethoxysilane and its co-hydrolysis with dimethyldiethoxysilane were carried out under variable reaction conditions: concentration of water, base or acid catalysts, temperature and solvent. The results, summarized in Table 5, show that the hydrolytic condensation can be carried out under both acid and base catalyzed conditions. At low concentration of water (~0.5 mol per 1 mol of diethoxysilane) the process led to formation of a dimer $[Me(EtO)(PhCH{=}CH)Si]_2O$. When an excess of water was used, the molecular weights of the oligomeric products were rather low and independent of the ratio $[monomer]/[H_2O]$ in the studied range. Progress of hydrolysis was followed by monitoring the relative intensities of the CH_3–Si/CH_3CH_2O

Table 4 Coupling of $Me(EtO)_2SiCH{=}CH_2$ with styrene

				Coupling products[a] (%)		
Styrene molar excess (%)	Catalyst (%wt)	Solvent	Reaction time/h	A	B	C
3	$RuCl(H)(CO)(PPh_3)_3$ (2)	toluene	19	11	7	75
10	$RuCl(SiMe_3)(CO)(PPh_3)_2$ (2)	toluene	21	5	3	89
400	$RuCl(H)(CO)(PPh_3)_3$ (1.5)	toluene	90	1	1	98
400	$RuCl(H)(CO)(PPh_3)_3$ (1)	—	90	0.5	0.5	99

[a] A – $Me(EtO)_2SiCH{=}CHSi(OEt)_2Me$ (*Z*); B – $Me(EtO)_2SiCH{=}CHSi(OEt)_2Me$ (*E*); C – $Me(EtO)_2SiCH{=}CHPh$ (*E*).

Table 5 Hydrolytic oligomerization of Me(EtO)$_2$SiCH=CHPh

[Me(EtO)$_2$SiCH=CHPh]/mol L^{-1}	[Me$_2$Si(OEt)$_2$]/mol L^{-1}	[H$_2$O]/mol L^{-1}	[Catalyst]/mol L^{-1}	Solvent	T/°C	Reaction time/h	M_n	M_w/M_n	ΣMe/CH$_3$CH$_2$O (^{1}H NMR)^a A	ΣMe/CH$_3$CH$_2$O (^{1}H NMR)^a B	ΣMe/–CH= (^{1}H NMR)^a A	ΣMe/–CH= (^{1}H NMR)^a B
0.80	—	0.40	H$_2$SiO$_4$ (0.001)	Et$_2$O	20	24	—	—	0.5	15.4	3.0	7.9
0.79	—	0.40	Me$_3$SiCl (0.31)	Et$_2$O	20	24	290	1.6	1.1	36.4	6.5	10.3
2.70	—	2.60	Me$_3$SiCl (1.08)	toluene	70	165	640	1.9	1.1	3.1	6.6	37.1
2.90	—	5.80	KOH (0.004)	toluene	70	115	613	1.8	0.5	2.8	3.0	3.3
0.86	0.37	8.95	Me$_3$SiCl (0.46)	Et$_2$O	20	100	260	1.7	1.0	246.6	10.4	9.6

[a] A – before reaction. [b] B – after reaction.

resonances in the ^{1}H NMR spectrum (at 0.32 and 1.29 ppm, respectively), and the structures of products were determined from the ratios of the CH_3–Si/Ph–CH= resonances (at 0.32 and 7.15 ppm). The degree of hydrolysis was larger in acid catalyzed reactions. H$_2$SO$_4$ was found to be more efficient than HCl generated from Me$_3$SiCl. The conversion of ethoxy groups increased a lot on increasing the ratio [H$_2$O]/[CH$_3$CH$_2$O–] (Table 5, entry 5; co-hydrolysis). However, acid catalysts apparently cleave off phenylethenyl groups in the condensation products. The ratio of CH_3–Si/Ph–CH= was higher than the theoretical value, and increased with the amount of acid used. The exception is hydrolytic co-polycondensation of methyl(phenylethenyl)diethoxysilane with dimethyldiethoxysilane, again carried out with an excess of water. Apparently the strength and molar concentration of an acid is more important in the studied system than the ratio of [–CH=CHPh]/[acid].

Conclusions

In this work we have presented a novel approach to the synthesis of oligo- and polysiloxanes bearing π-conjugated phenylethenyl substituents at silicon atoms. Silicone fluids of this structure are for the first time obtained by effective coupling of vinyl-Si moieties and styrenes in the presence of ruthenium complexes yielding a cost effective alternative to the hydrosilylation pathway. The products exhibit refractive indices ranging from 1.51 to 1.59 (depending on the content of PhCH=CH– moieties), which is a substantial increase from the 1.40 value for simple PDMS. Two synthetic pathways were developed based either on coupling of cyclic and linear vinylsiloxanes with styrene (or α-methylstyrene) or involving preliminary synthesis of a difunctional monomer, such as methyl(phenylethenyl)diethoxysilane, which was further used in a hydrolytic condensation reaction. Catalytic activity of transition metal complexes was thoroughly re-examined. The most effective catalysts proved to be those promoting the silylative coupling reaction pathway, [RuCl(H)(CO)(PPh$_3$)$_3$] and [RuCl(SiMe$_3$)(CO)(PPh$_3$)$_2$], while metallacarbene complexes of ruthenium and molybdenum gave poor yields. Contrary to earlier reports concerning styrene coupling with simple vinylsilanes, ruthenium complexes such as [RuCl$_2$(PPh$_3$)$_3$] and [Ru(OAc)(H)(CO)(PPh$_3$)$_2$] proved to be ineffective in coupling styrenes with oligo- and polyvinylsiloxanes. Additionally, it has been found that styrene polymerization, which surprisingly seems not to have been reported earlier, occurs as a side reaction during silylative coupling. This side reaction of radical styrene polymerization can be limited or avoided by the use of such quenchers as hydroquinone, 4-*tert*-butylcatechol or 2,6-di-*tert*-butyl-4-methylphenol. It was also noted that the addition of radical quenchers increases the yield of coupling presumably limiting the decay of the active ruthenium species.

Acknowledgements

This work was supported by GE Silicones, General Electric Company, and by KBN Polish State Committee for Research, Grant PBZ-KBN/01/CD/00.

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