Electronic Supplementary Information

A metal-free radical technique for cross-linking of polymethylhydrosiloxane or polymethylvinylsiloxane using AIBN

Konstantin V. Deriabin, Mikhail V. Dobrynin and Regina M. Islamova*

Institute of Chemistry, Saint Petersburg State University, 7/9 Universitetskaya Nab., 199034 Saint Petersburg, Russia

**Corresponding author: Regina M. Islamova, e-mail: r.islamova@spbu.ru*

Table of contents

1. Materials

α,ω-di(trimethylsiloxy)polymethylhydrosiloxane (**PMHS**, M_n=1700–3200 g/mol, viscosity 12–45 cSt, Aldrich), α,ω-di(trimethylsiloxy)poly(methylhydrosiloxane-*co*-dimethylsiloxanes (**PMHS-*co*-PDMS-a**, 25–35% Si–H, viscosity 25–35 cSt, M_n≈950 g/mol, ABCR), α,ω-di(trimethylsiloxy)poly(methylhydrosiloxane-*co*-dimethylsiloxane) (**PMHS-*co*-PDMS-b**, 5–7% Si–H, viscosity 9000–11000 cSt, ABCR), α,ω-di(trimethylsiloxy)polydimethylsiloxane (**PDMS**, M_n=50000 g/mol, Aldrich), poly(vinylmethylsiloxane) (**PMVS**, 99.9% vinyl groups, viscosity 3–7 cSt, ABCR), octamethylcyclotetrasiloxane D-4 (98%, Aldrich) and hexavinyldisiloxane (95%, ABCR) were purchased from commercial suppliers and used as received. Azobisisobutyronitrile (**AIBN**, 98%, Aldrich) was recrystallized from ethanol twice before usage.

2. Characterizations

NMR spectra were recorded on a commercial instrument (400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C, 79.50 MHz for ^{29}Si) in $CDCl_3$. Chemical shifts are given in δ-values [ppm] referenced to the residual signals of non-deuterated solvent ($CHCl_3$): δ 7.26 (^{1}H) and 77.2 (^{13}C).

SSNMR spectra were obtained using either a Bruker Avance III WB 400 operating at 400.23 MHz for ^{1}H (16 scans), 100.64 MHz for ^{13}C (2000 scans) and 79.51 MHz for ^{29}Si (2000 scans). They were obtained under magic-angle spinning conditions with spin-rates around 12500 Hz. ^{13}C and ^{29}Si SSNMR spectra were recorded with cross-polarization (typically with a recycle delay of 2.0 s and a contact time of 2.00 ms) and direct excitation (typically with a recycle delay of 5.0 s) with ^{1}H decoupling. ^{1}H spectra were obtained with direct excitation. Samples were run as-prepared and spectral referencing is with respect to external, neat tetramethylsilane.

3. Synthesis of PDMS-v

α,ω-di(trivinylsiloxy)polydimethylsiloxane (**PDMS-v**) was prepared by the alkaline polymerization of octamethylcyclotetrasiloxane D-4 with hexavinyldisiloxane by the procedure,[1,2] was transparent liquid polymer with viscosity of 96 cSt. ^{1}H NMR spectra, δ, ppm: –0.11–0.29 br.s (3H, CH_3Si), 5.77–5.95 m (1H, $CH_2{=}CHSi$), 6.02–6.23 m (2H, $CH_2{=}CHSi$). The content of vinyl groups, according to ^{1}H NMR data, is 1.3 mol %. The number-average molecular weight M_n=33000 g/mol and the weight-average molecular weight M_w=80000 g/mol.

4. General curing procedure

The cross-linking of polysiloxanes was carried out in aluminum crucibles with **AIBN** as curing agent at temperature range 80–120 °C in a thermostat (heating chamber without forced convection). Concentrations of **AIBN** were 0.1–0.6 M. A calculated amount of **AIBN** was mixed with polysiloxane (1 g of **PMHS**, **PMHS-co-PDMS-a**, **PMHS-co-PDMS-b**, **PDMS-v**, **PMVS** or **PDMS**) until white mixture obtained. In case of **PMHS** and **PMVS** polymer concentration was 0.3 M and 0.8 M, respectively. The newly-prepared mixtures for thermal curing were placed in a thermostat and heated to the required temperature. It was necessary to gradually warm the mixture to the curing temperature in order to dissolve **AIBN** and until homogenization occurred. *Caution: heating of large amounts of **AIBN** can lead to explosion. The fine powder of **AIBN** is prone to forming aerosols.*

The curing time (τ_{curing}) was visually defined as the time period from the moment of placing the aluminum crucible, which contains a mixture of polysiloxane and initiator, into the thermostat at the required temperature until cured rubber was formed. Curing times were measured as dry-to-touch times according to ASTM D1640.[3] All the above experiments regarding the measurement of curing times were carried out three times for each sample.

5. Swelling experiments

For swelling measurements, a representative sample of silicone rubber (0.070 g, round disk) was weighed for evaluating the initial dry weight (m_{unex}), swollen for 2 hours in Soxhlet apparatus in benzene (boiling point 80 °C), gently wiped to remove liquid solvent on the sample surface and weighed (m_s). After that the sample was dried for 24 hours at room temperature and 12 hours at 60 °C and weighed again (m_{ex}). The soluble fraction (w_{sol}) and volume fraction of polymer in the swollen sample (υ) were obtained according to formulae:

$$w_{sol}(\%) = \frac{m_{unex} - m_{ex}}{m_{unex}} \times 100 \qquad (1)$$

$$v = \left[1 + \frac{m_s - m_{ex}}{m_{ex}} \times \frac{\rho_p}{\rho_s}\right]^{-1} \qquad (2)$$

In (1) and (2) ρ_s and ρ_p are the solvent (benzene, 0.879 g/cm^3) and polymer (**PMHS**, 1.006 g/cm^3 or **PMVS**, 0.990 g/cm^3) densities, respectively. Swelling experiments were carried out five times for each test.

6. NMR spectra

6.1. PMHS

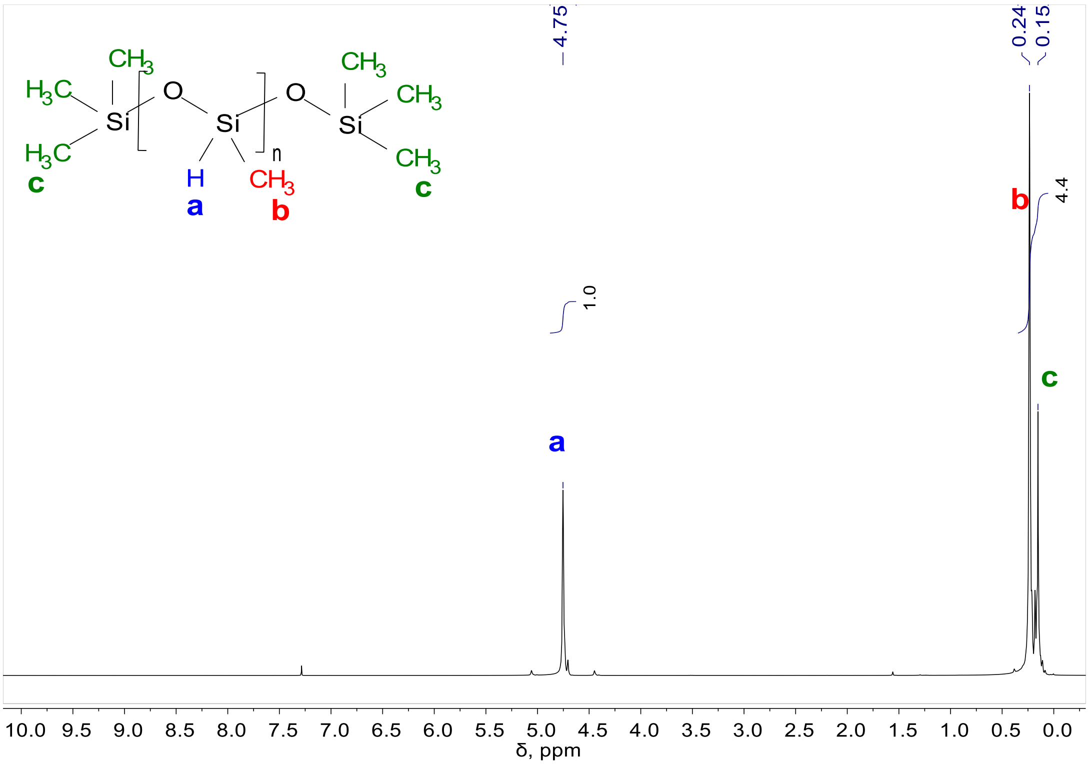


Fig. 1S. The ^{1}H NMR of **PMHS** (before cross-linking).

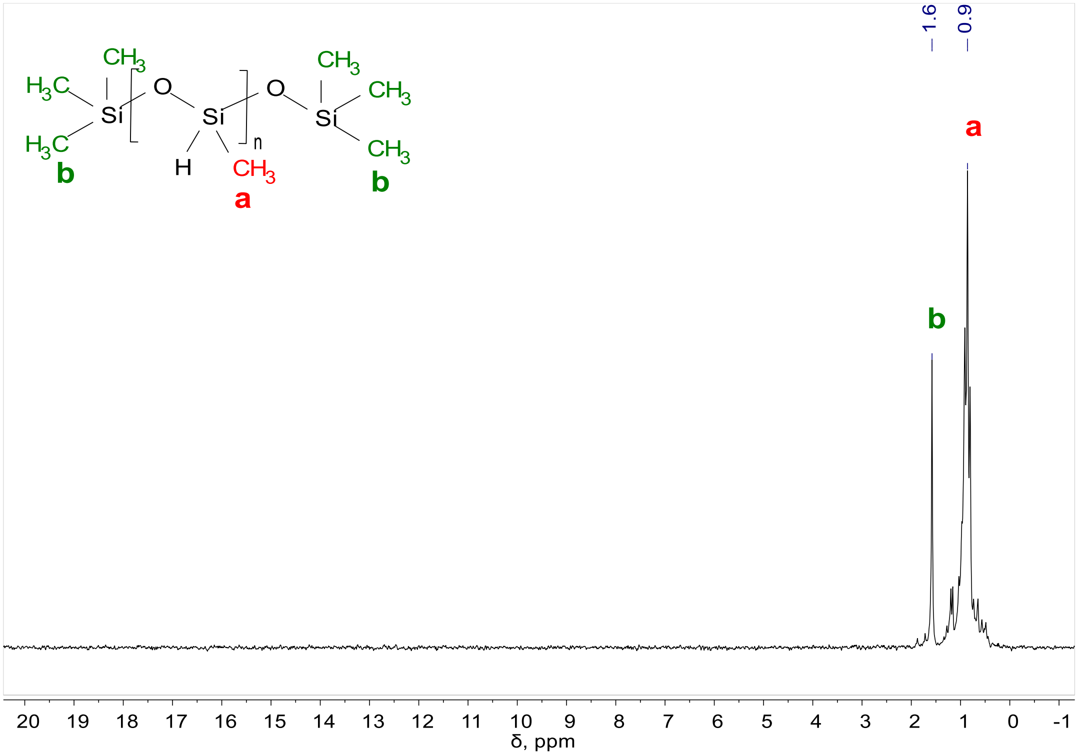


Fig. 2S. The ^{13}C NMR of **PMHS** (before cross-linking).

*6.2. Cured **PMHS***

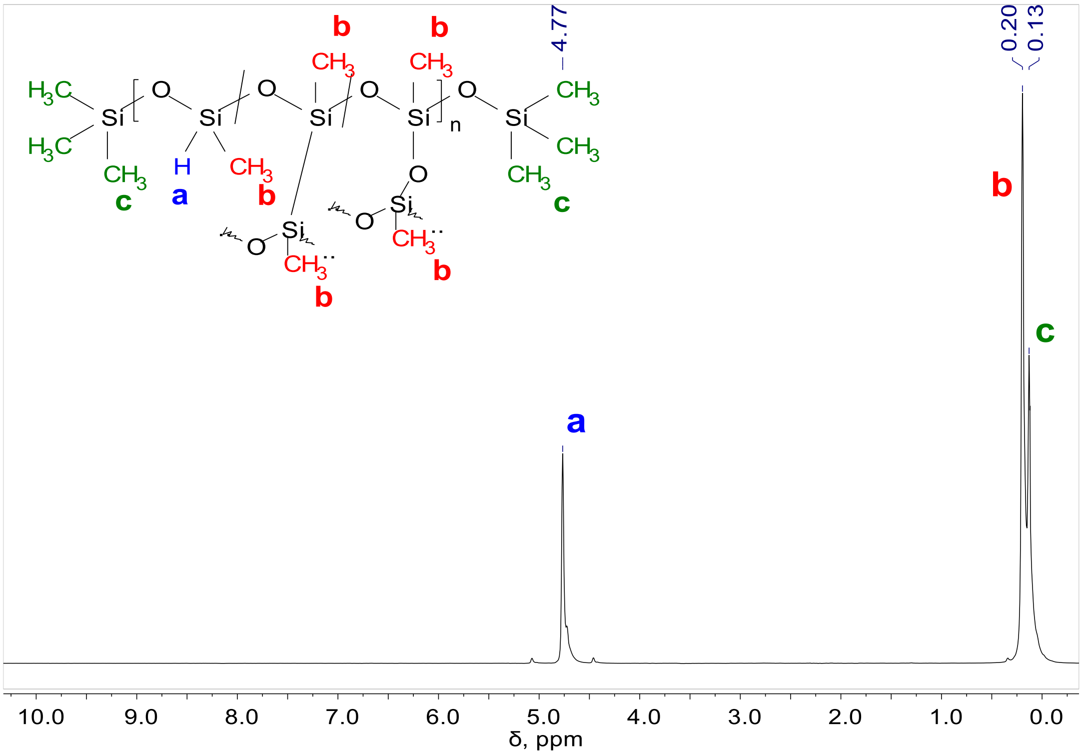


Fig. 3S. The ^{1}H SSNMR of cured **PMHS** by 0.2 M **AIBN**.

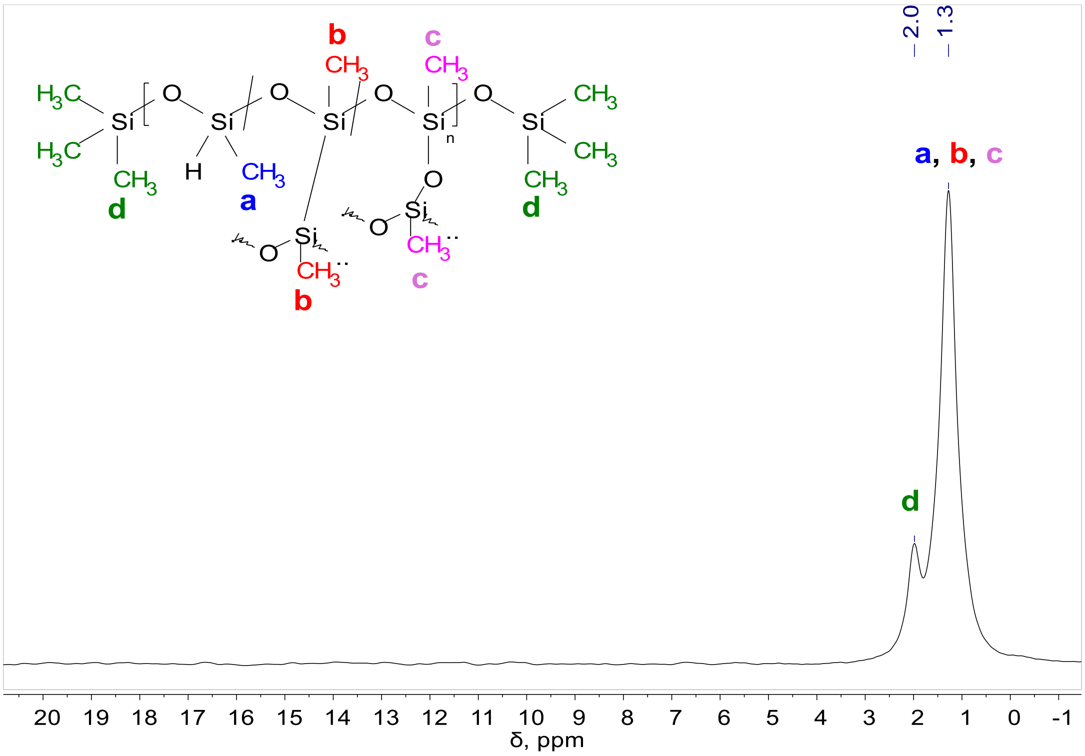


Fig. 4S. The ^{13}C SSNMR of cured **PMHS** by 0.2 M **AIBN**.

6.3. PMVS

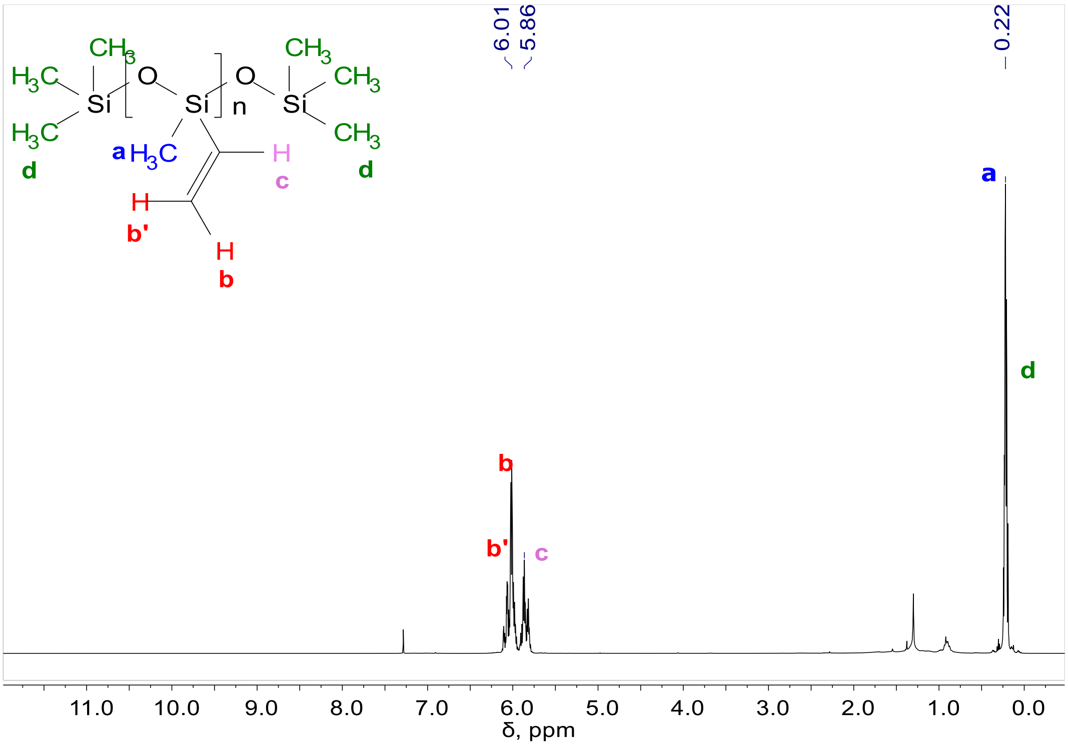


Fig. 5S. The ^{1}H NMR of **PMVS** (before cross-linking).

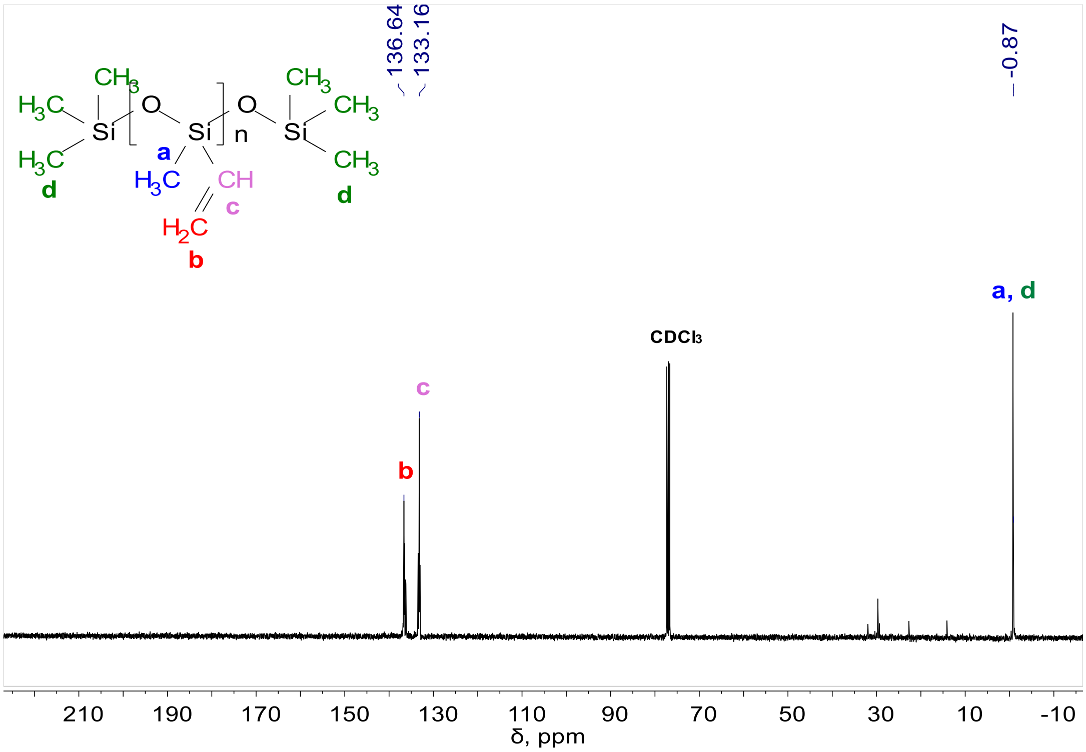


Fig. 6S. The ^{13}C NMR of **PMVS** (before cross-linking).

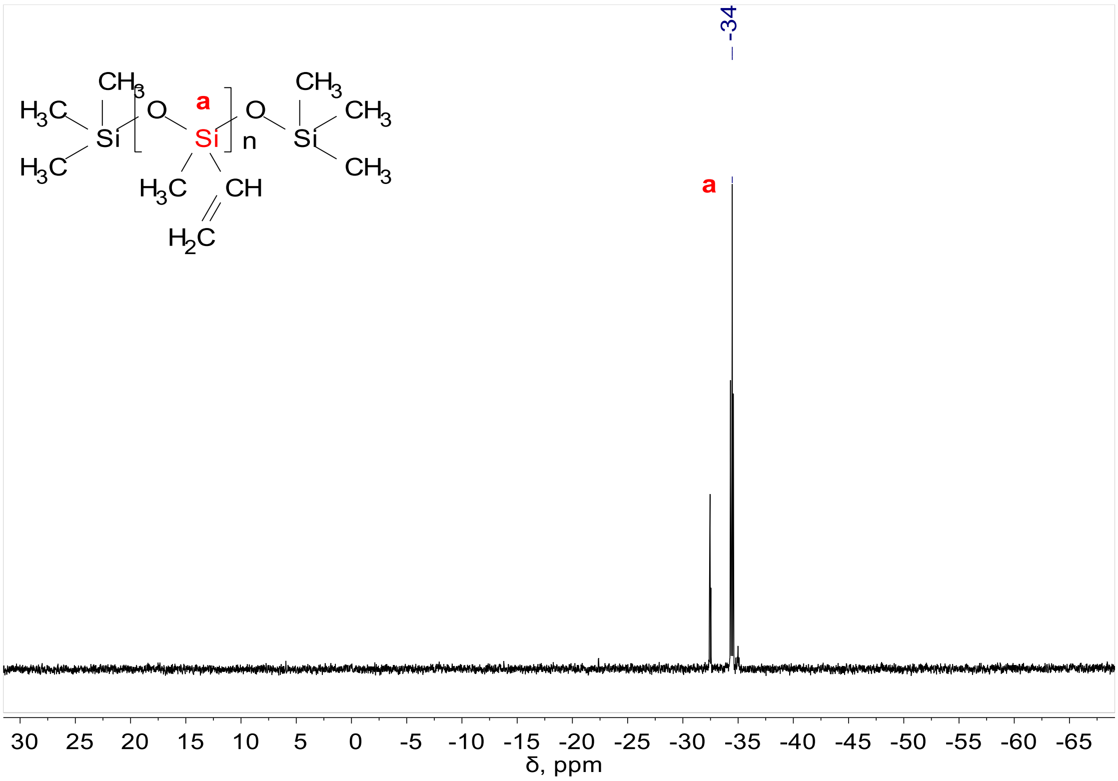


Fig. 7S. The ^{29}Si NMR of **PMVS** (before cross-linking).

*6.4. Cured **PMVS***

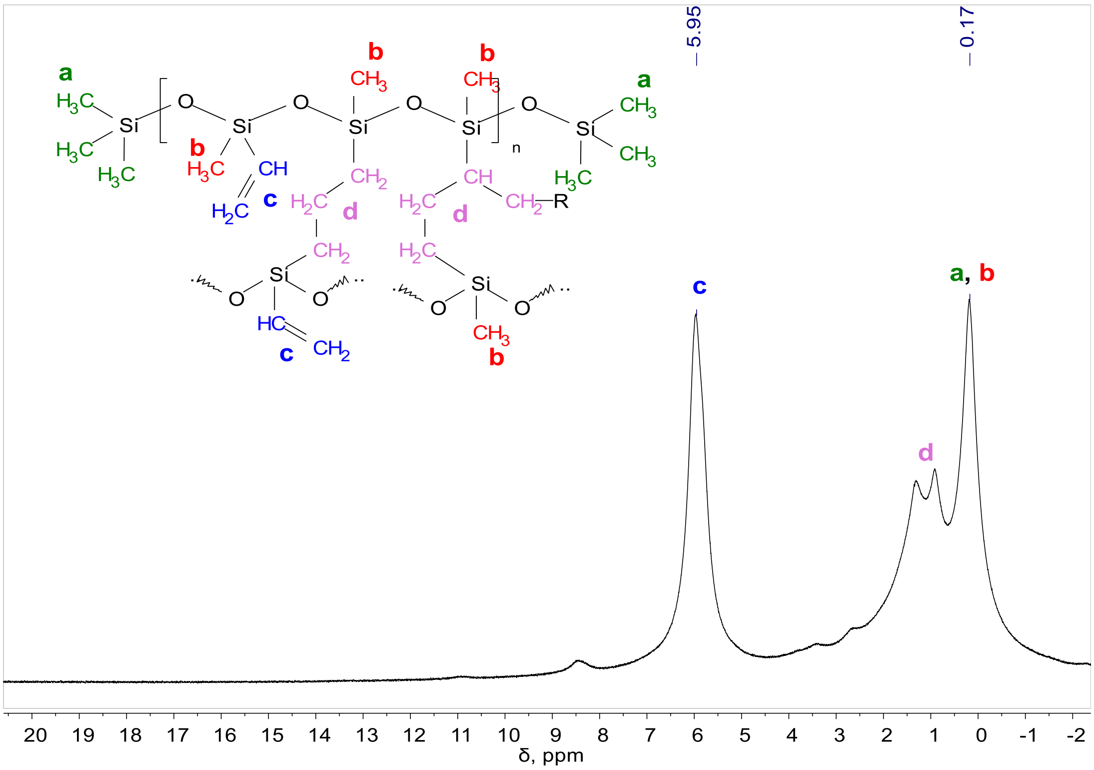


Fig. 8S. The ^1H SSNMR of cured **PMVS** by 0.6 M **AIBN**.

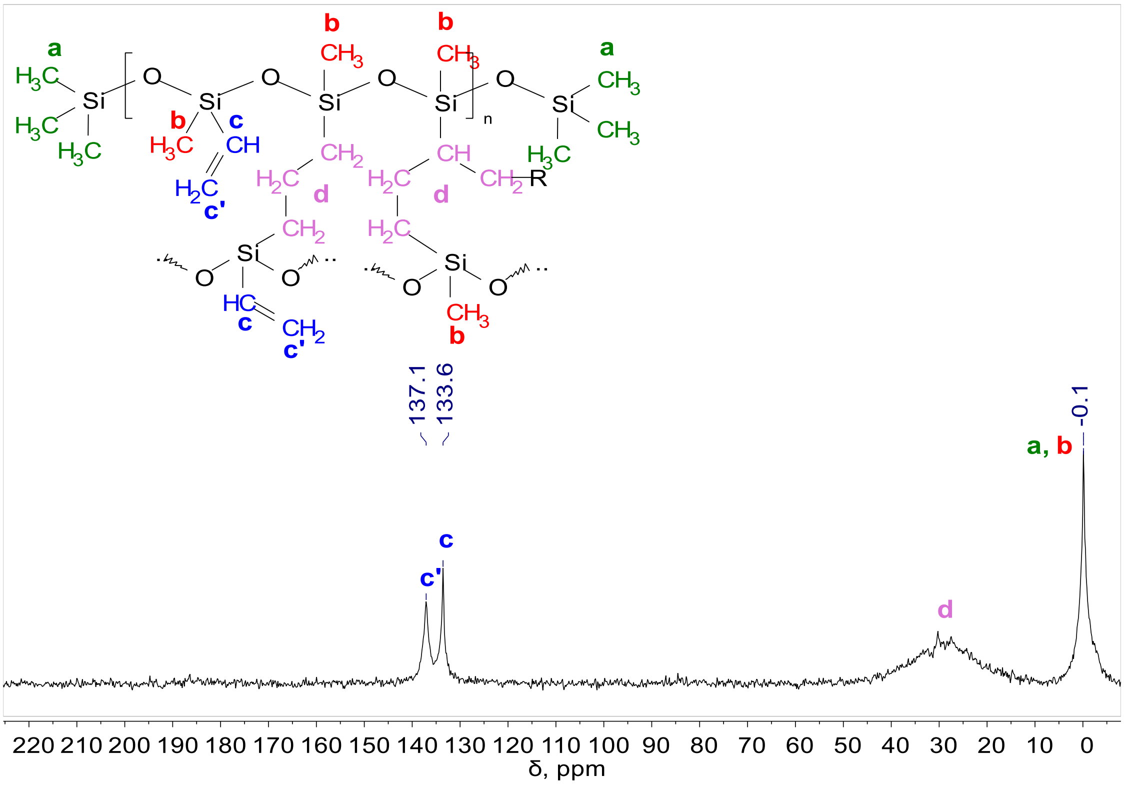


Fig. 9S. The ^{13}C SSNMR of cured **PMVS** by 0.6 M **AIBN**.

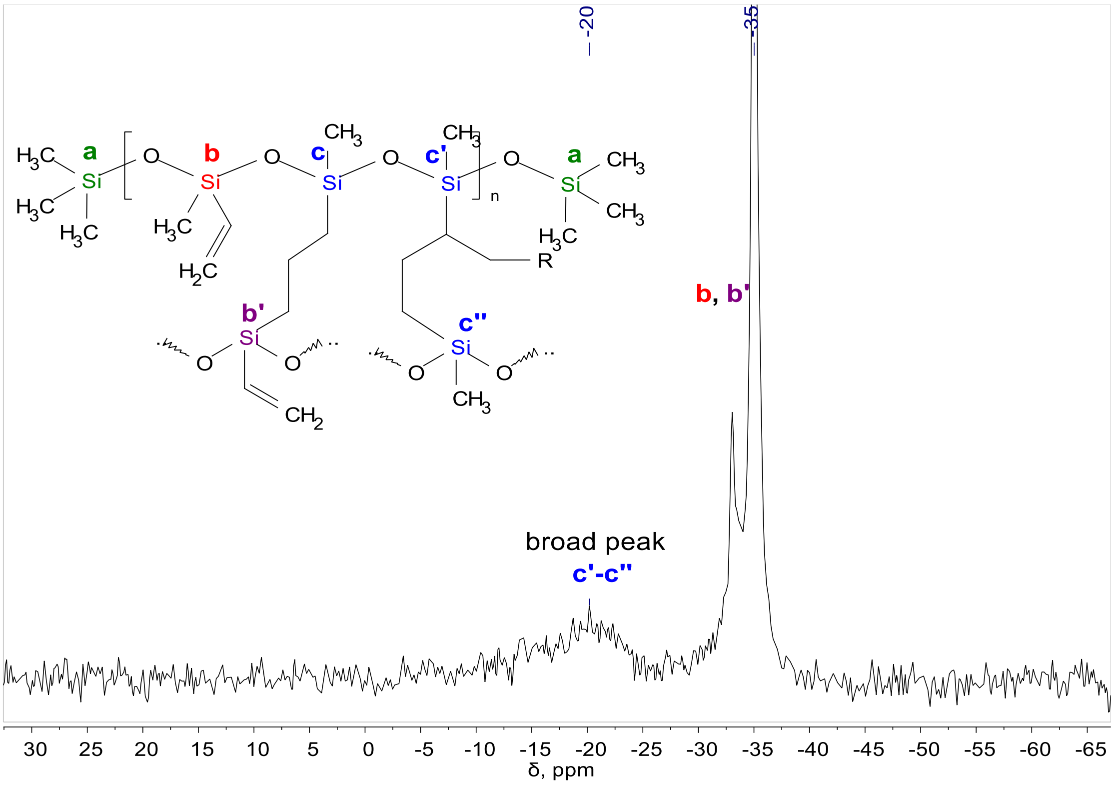


Fig. 10S. The ^{29}Si SSNMR of cured **PMVS** by 0.6 M **AIBN**.

6.5. ***PDMS-v/PMHS mixture***

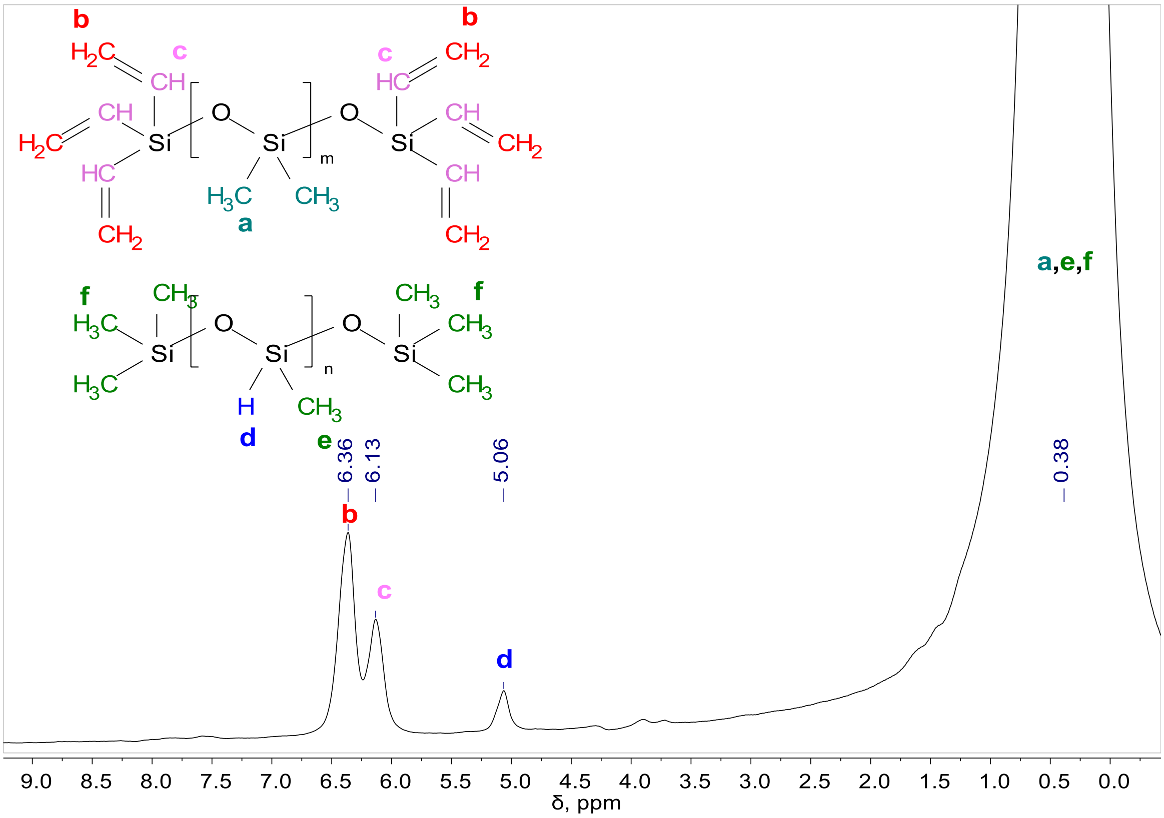


Fig. 11S. The ^{1}H SSNMR of **PDMS-v/PMHS mixture**.

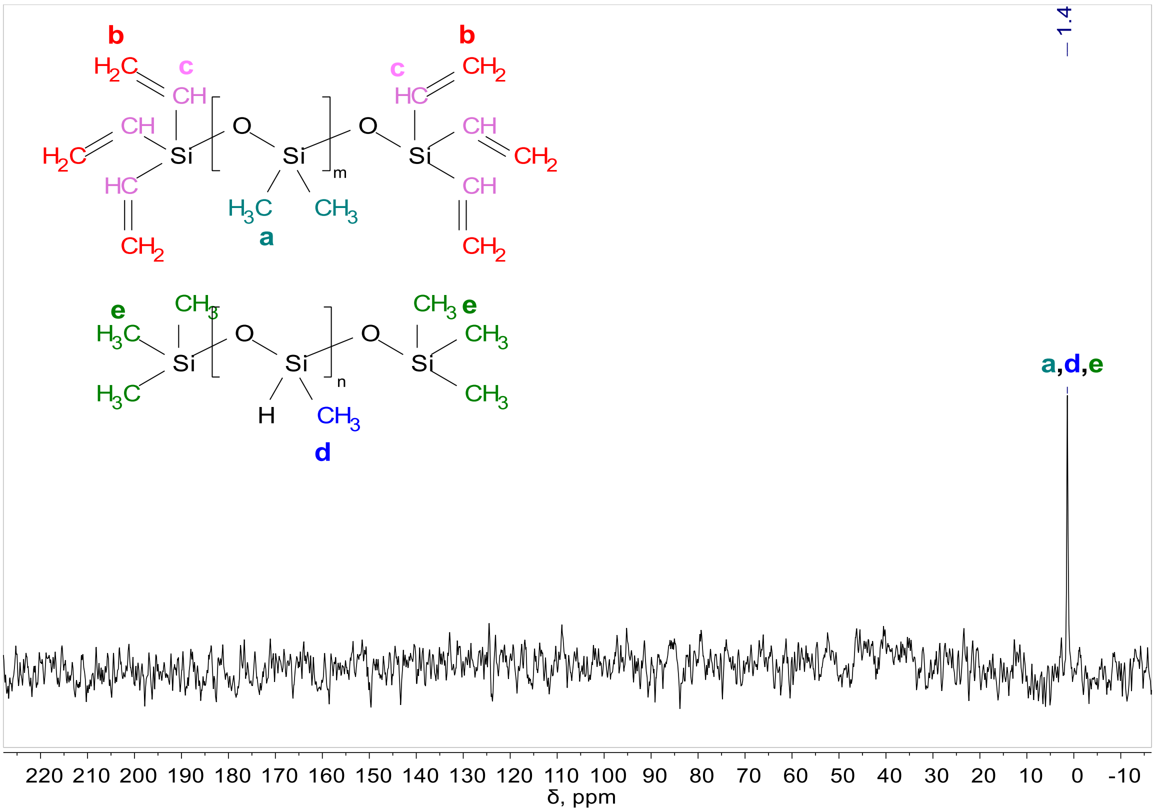


Fig. 12S. The ^{13}C SSNMR of **PDMS-v/PMHS mixture**.

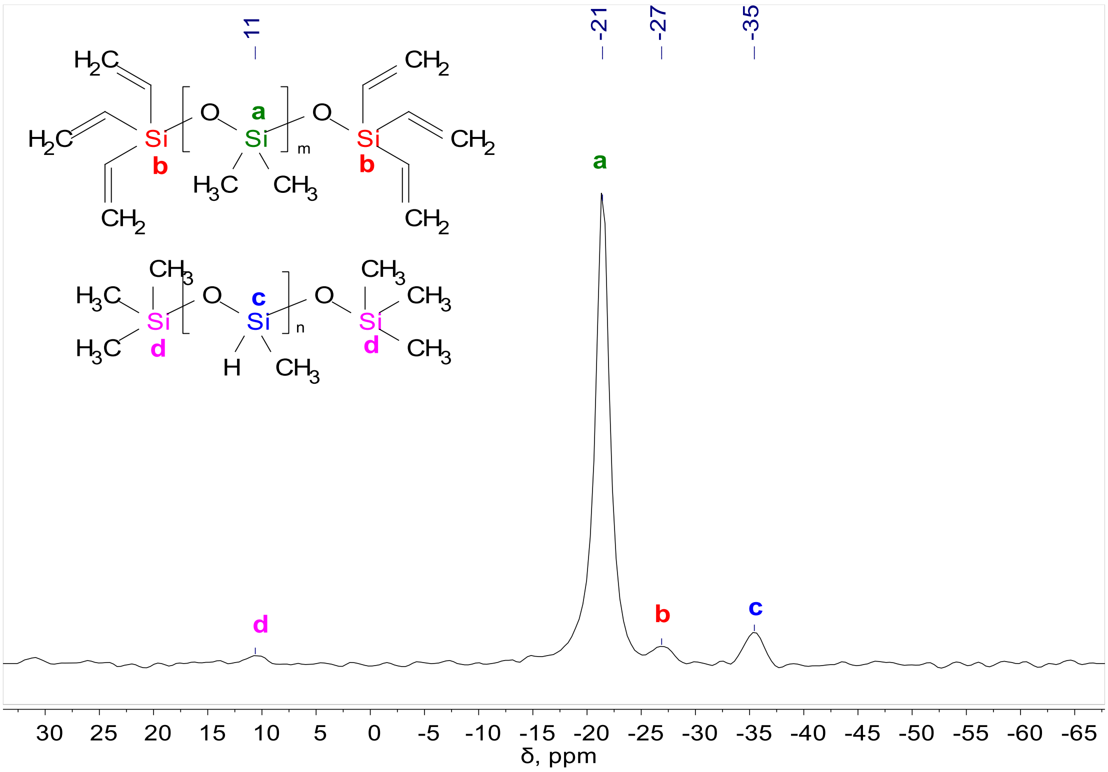


Fig. 13S. The ^{29}Si SSNMR of **PDMS-v/PMHS mixture**.

*6.6. Cured **PDMS-v/PMHS mixture***

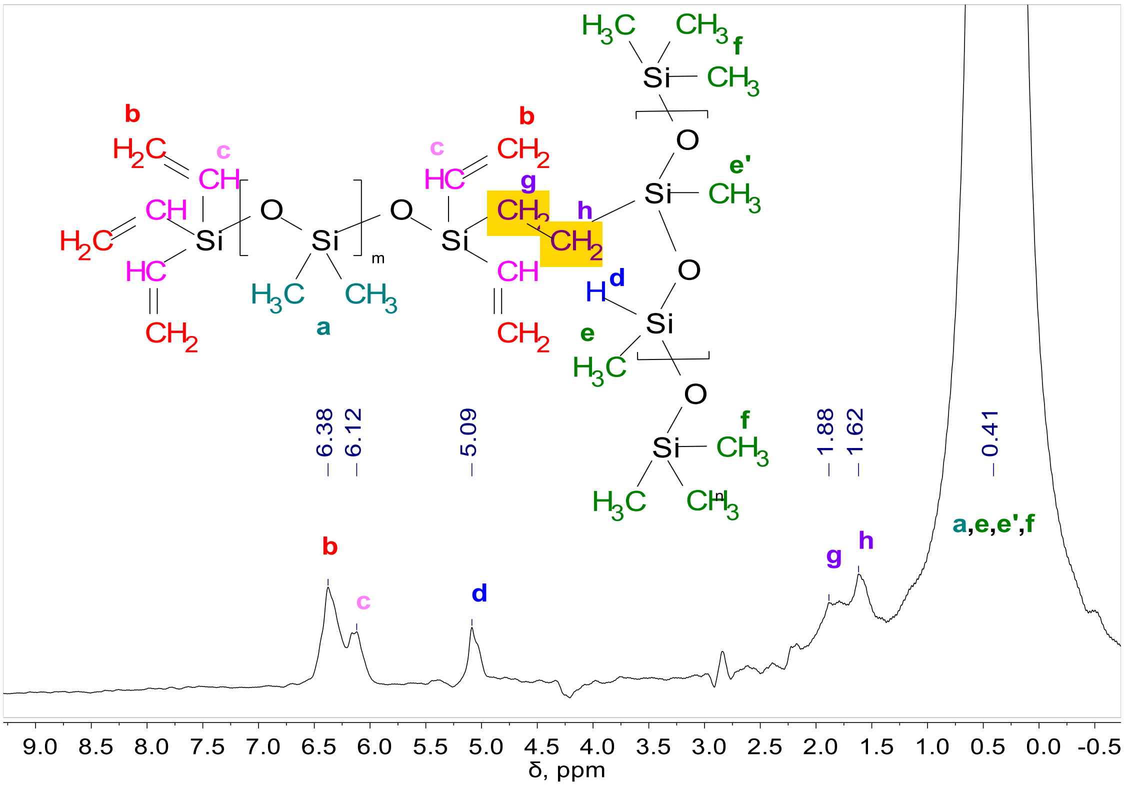


Fig. 14S. The ^{1}H SSNMR of cured **PDMS-v/PMHS mixture**.

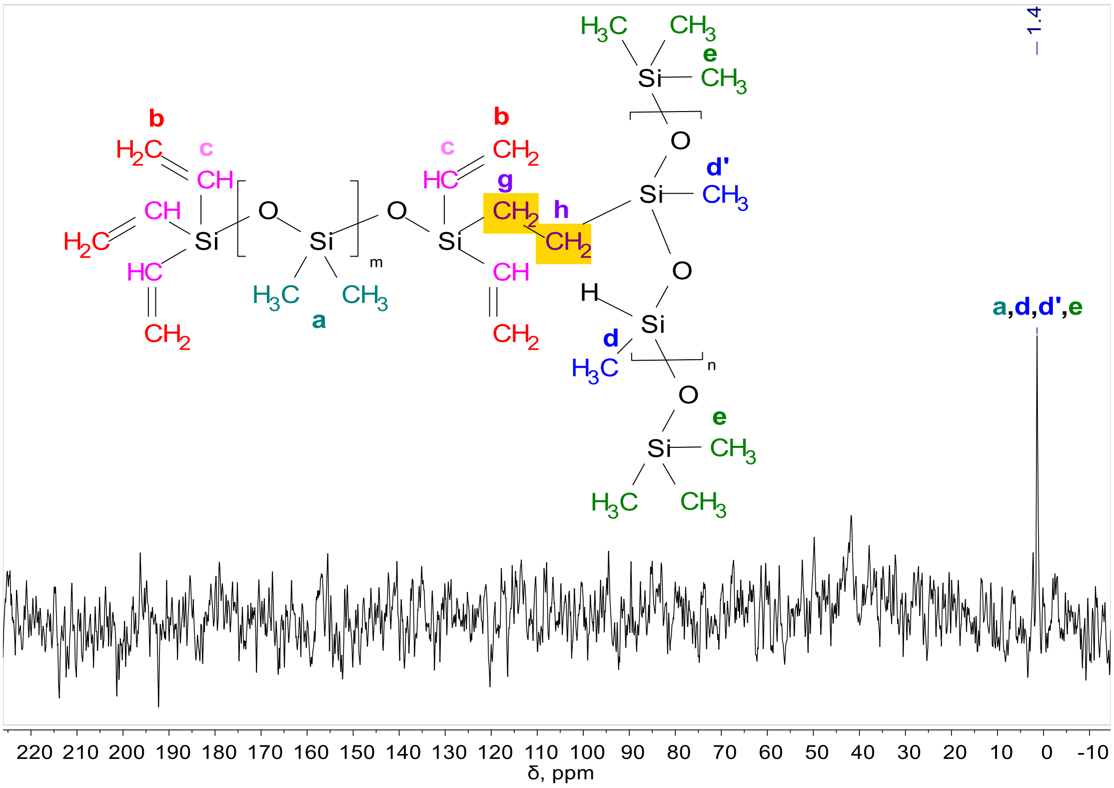


Fig. 15S. The ^{13}C SSNMR of cured **PDMS-v/PMHS mixture**.

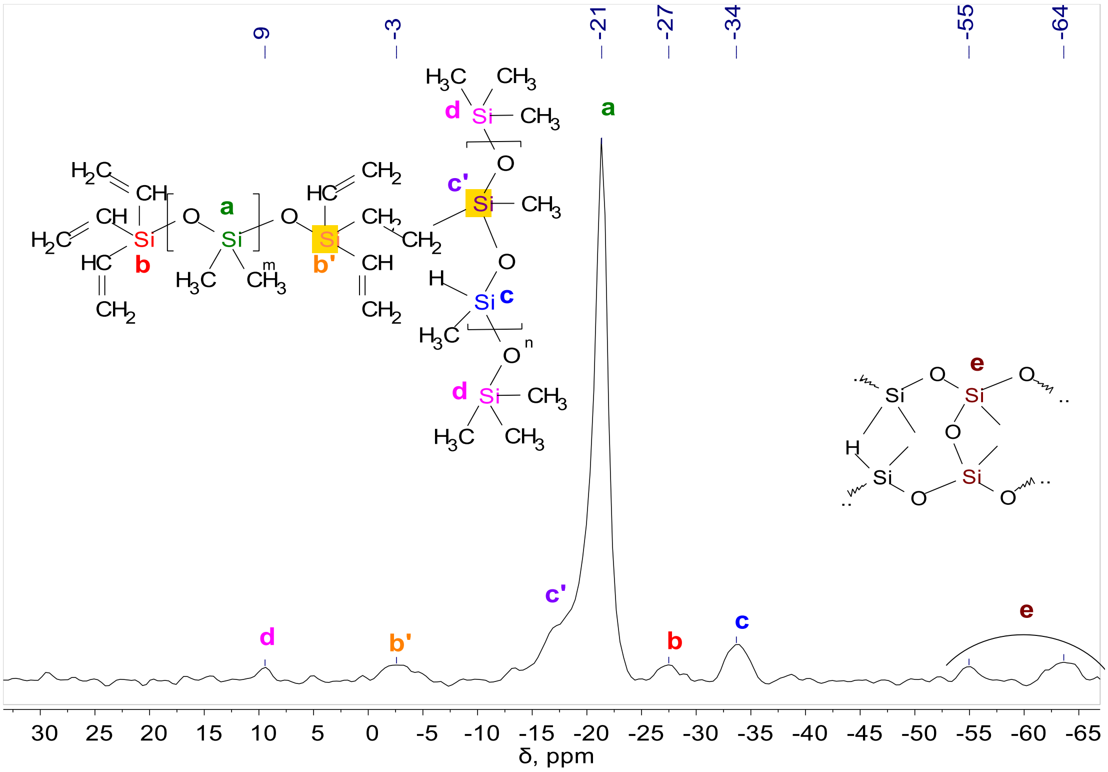
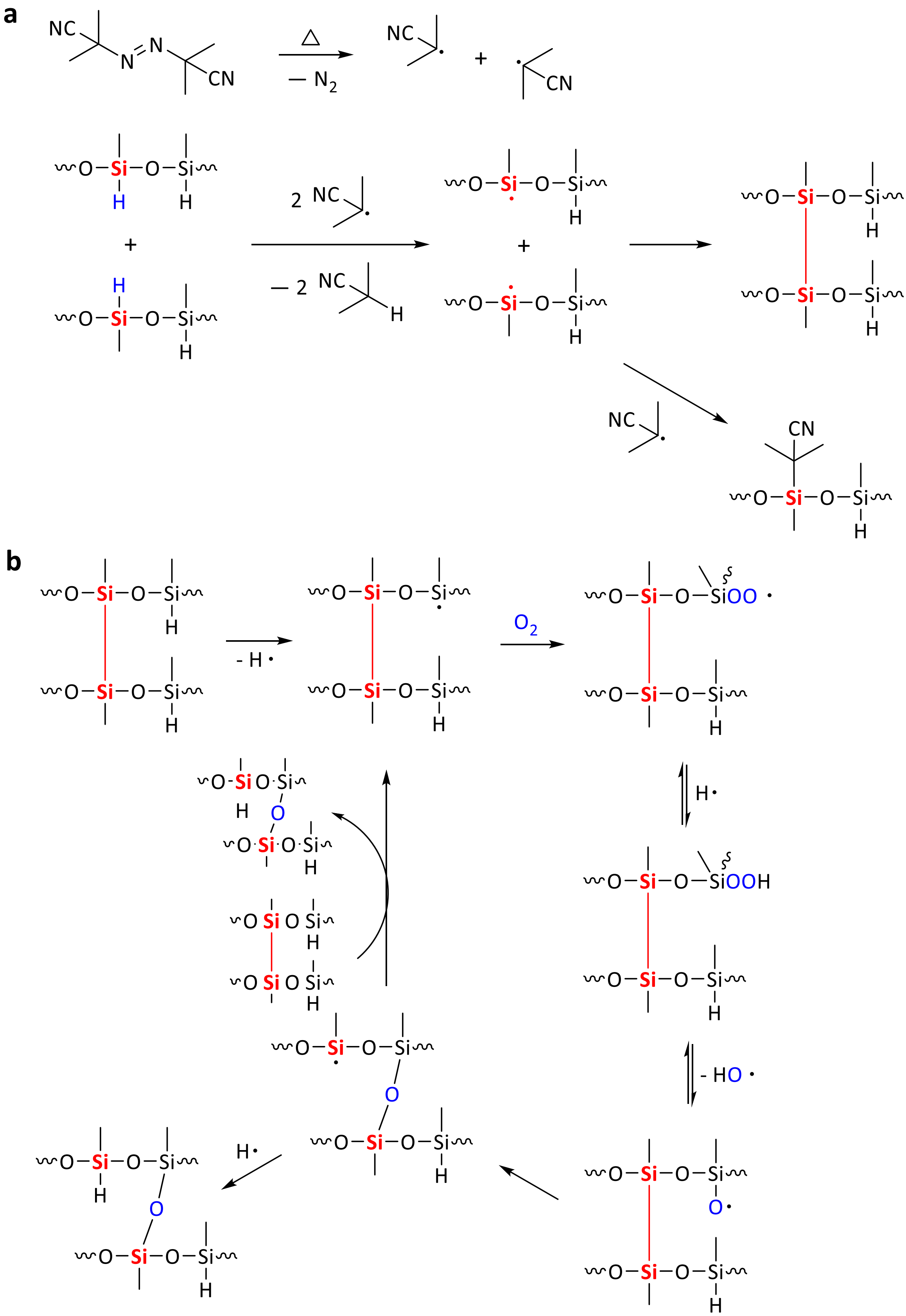


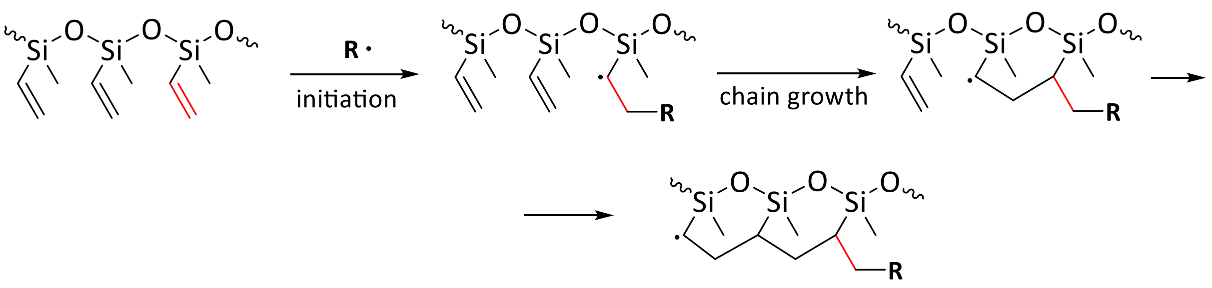
Fig. 16S. The ^{29}Si SSNMR of cured **PDMS-v/PMHS mixture**.

7. Possible mechanisms of PMHS and PMVS cross-links formation

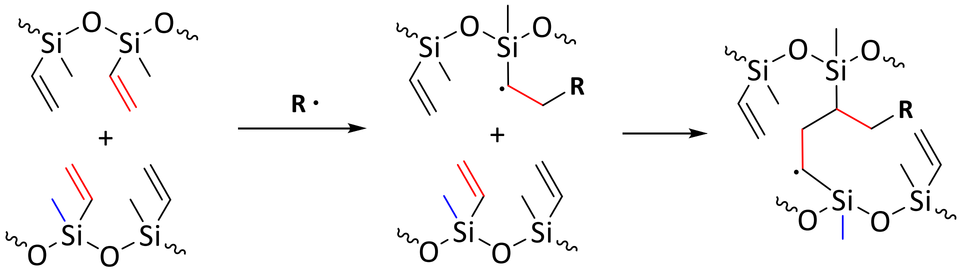


Scheme 1S. Proposed mechanism of Si–Si radical coupling [4–9] (**a**) and mechanism of autoxidation [10,11] (**b**).

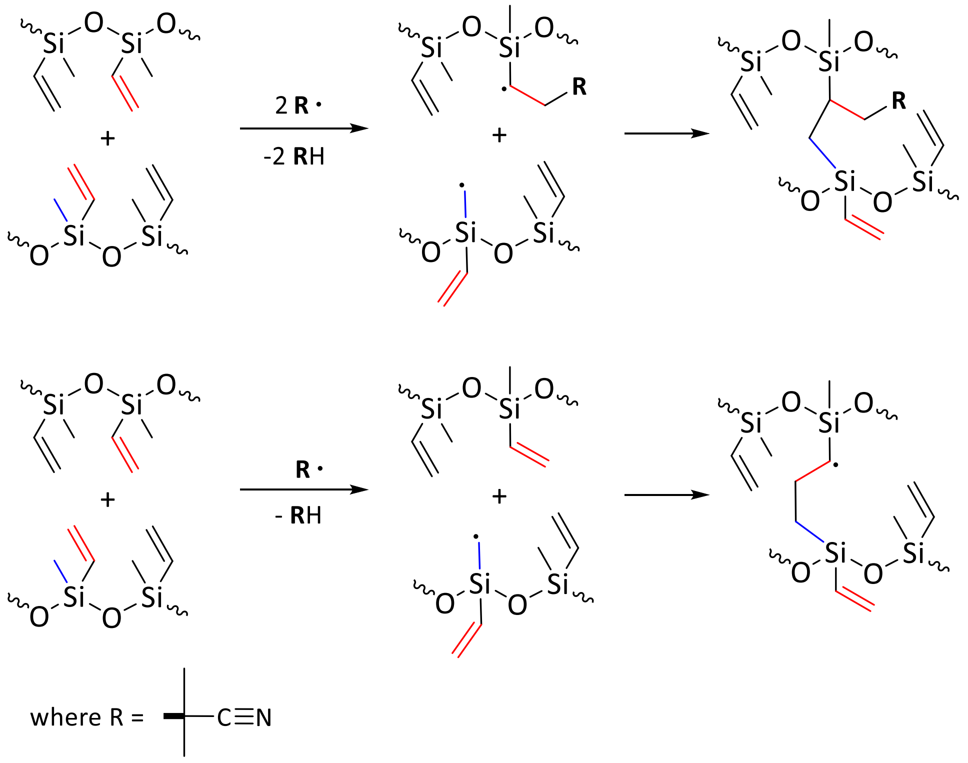
1. intramolecular polymerization - no cross-linking



2. "vinyl-vinyl"



3. "vinyl-methyl"



Scheme 2S. Proposed mechanisms of **PMVS** cross-linking.[12,13]

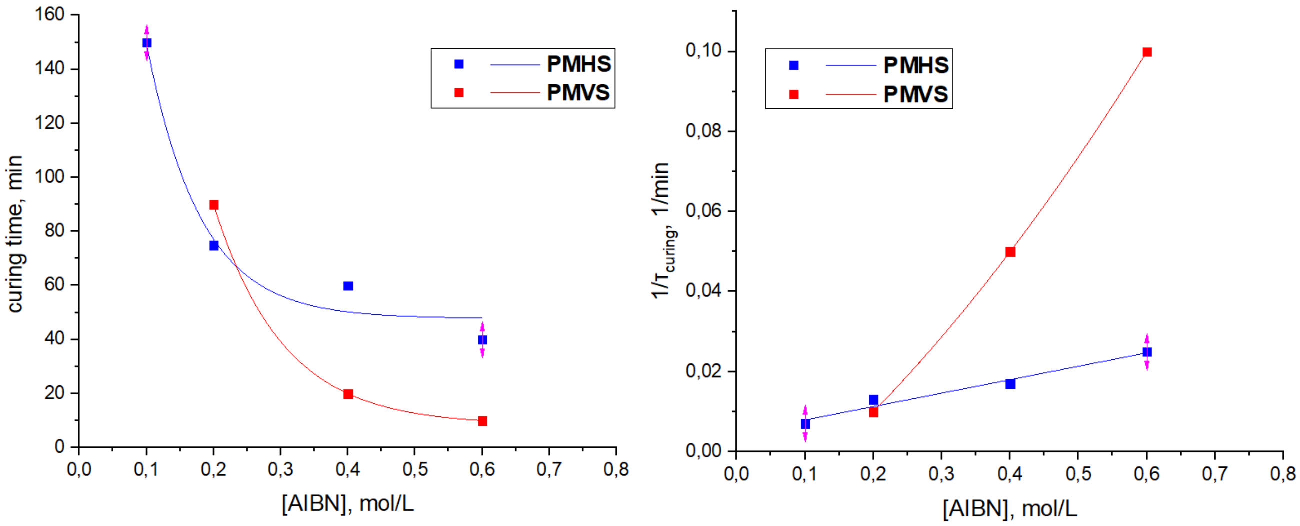


Fig. 17S. Plots of curing time dependence on **AIBN** concentration.

As distinguished from **PMHS**, the mechanism of **PMVS** radical curing includes a lot of competing reactions.[12–13] We believe that not only “vinyl-to-vinyl” and “vinyl-to-methyl” reactions but also an intramolecular polymerization of side vinyl groups occurs during curing process. The last one does not participate in the **PMVS** cross-linking due to easy steric availability of side vinyl groups.

The intramolecular polymerization directly influences on curing rate. This aspect inhibits cross-linking process if a small amount of **AIBN** (0.1 M) is used. In this case, **AIBN** probably acts as initiator for polymerization of vinyl groups. On the other hand, large quantities of **AIBN** (>0.2 M) lead to cross-linking *via* intermolecular reactions (“vinyl-to-vinyl” and “vinyl-to-methyl”) because this amount will be enough to initiate such processes along with polymerization. Therefore, the curing time extremely declines with **AIBN** concentration increasing for **PMVS** curing.

8. Degree of conversion for Si–H and vinyl groups: comparison of PMHS and PMVS

The degree of the Si–H conversion is calculated by comparison of the Si–H integrals in ^{1}H NMR spectrum for **PMHS** and ^{1}H SSNMR cross-linked **PMHS** by 0.2 M **AIBN** (eq. 3). Thus, **4.35%** of the Si-H groups reacted leading to the Si–Si and Si–O–Si cross-links (Fig. 11S).

$$\eta = \left(1 - \frac{\int remaining\ SiH\ after\ curing}{\int initial\ SiH\ before\ curing}\right) \cdot 100\% = \left(1 - \frac{0.22}{0.23}\right) \cdot 100\% = 4.35\% \qquad \text{(eq. 3)}$$

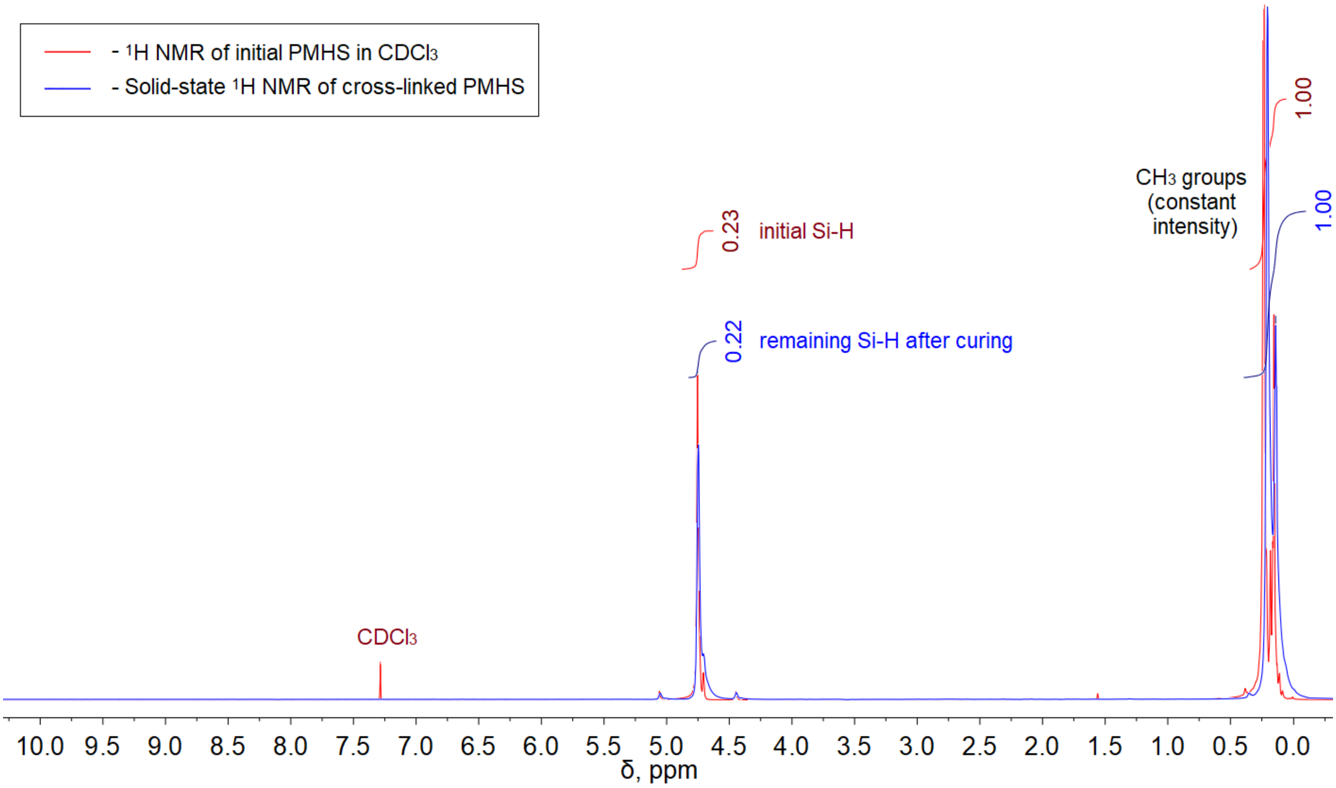


Fig. 18S. The 1H NMR of **PMHS** before and after the cross-linking initiated by 0.2 M **AIBN**.

In case of **PMVS** calculations yielded the result that ca. **23.40%** of vinyl groups reacted. In order to find cross-linking degree for **PMVS** from ^{1}H NMR, the integrals of vinyl groups are compared in ^{1}H NMR spectrum for **PMVS** and ^{1}H SSNMR cross-linked **PMVS** by 0.6 M **AIBN** (Fig. 12S, eq. 4):

$$\eta = \left(1 - \frac{\int remaining\ vinyl\ groups\ after\ curing}{\int initial\ vinyl\ groups\ before\ curing}\right) \cdot 100\% = \left(1 - \frac{0.72}{0.94}\right) \cdot 100\% = 23.40\% \qquad \text{(eq. 4)}$$

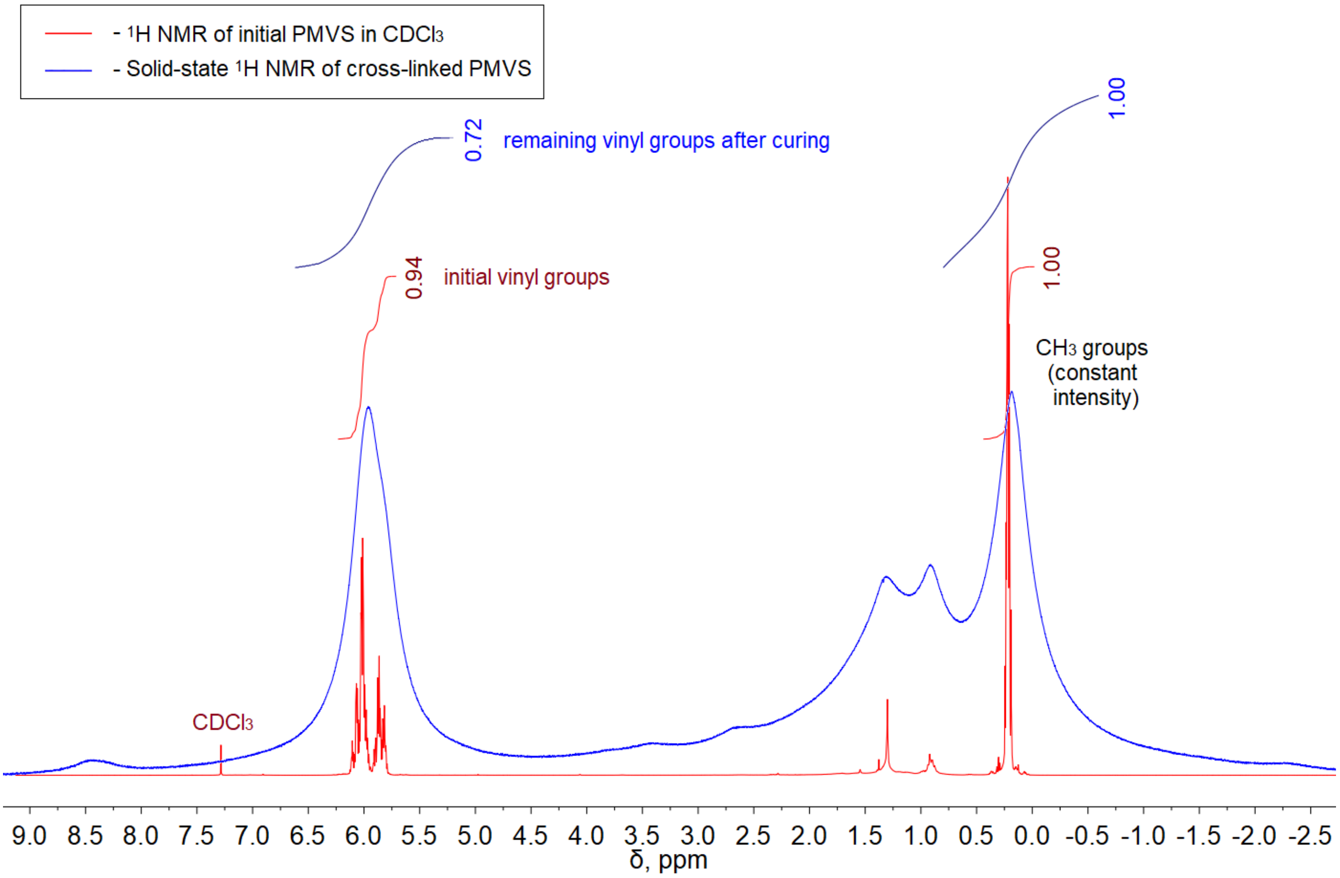


Fig. 19S. The ^{1}H NMR of **PMVS** before and after cross-linking initiated by 0.6 M **AIBN**.

Thus, the degree of conversion of vinyl groups in **PMVS** (23.40 %) is more than degree of the Si–H conversion in case of **PMHS** (4.35 %). Swelling degree in case of **PMVS** is substantially less (30%) compared to **PMHS** (220%) that agrees with calculations by ^{1}H NMR.

9. Notes and references

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