

Synthesis and thermoelastic characterization of PDMSM networks

K.H. Schimmel* and Pham the Trinh

Department of Chemistry, Technical University Leuna-Merseburg, DDR-4200 Merseburg,
German Democratic Republic

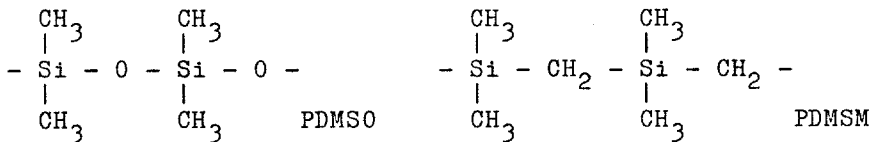
Summary

The synthesis of poly(dimethyl silmethylenes) with two hydroxyl endgroups is described. Networks produced by end-linking with tetraethoxysilane were characterized, and thermoelastic data were estimated. f_e/f and $\ln\langle L^2 \rangle_0/dT$ of these networks are much smaller than those of poly(dimethyl siloxanes).

Introduction

The understanding of the elastic properties exhibited by elastomer networks has been under investigation for a long time. The first molecular rubber theories of rubber elasticity dealt with either an idealized phantom network or a network in which the junction points move linearly with the macroscopic dimension of the sample. A great improvement in the experimental testing of these theories is the use of model networks. The specific chemical reactions used in their preparation lead to some quantitative information, e.g. about the molecular weight between crosslinking points and the functionality of the crosslinks.

Poly(dimethyl siloxane) PDMSO is a good example of a polymer which forms elastomeric networks that are inherently weak. The substitution of the oxygen atoms in the alternating silicon-oxygen chain of PDMSO by the methylene group leads to another polymer, poly(dimethyl silmethylene) PDMSM. This polymer consist of only silicon atoms and two groups, methyl and methylene, which are nearly identical in the way in which they affect the configurations of a chain molecule. In this sense it is a simpler molecule than poly-(dimethyl siloxane):



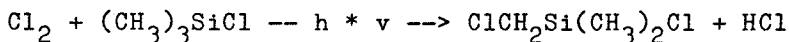
* To whom offprint requests should be sent

The comparison of the elastomeric properties of PDMSO with PDMSM will be interesting in case of the same network structure and comparable molecular masses between the junction points. MARK and others had studied the stress-optical behaviour [1] and configuration dependent properties [2] of PDMSM networks crosslinked by irradiation. Our investigations of PDMSM were carried out on end linked dihydroxyterminated poly(silmethylenes) of different molecular masses.

Synthesis of linear PDMSM chains and crosslinking reaction

The end-linking of polymers is the best way to prepare model networks. In our case, we had to synthesize poly(silmethylenes) with hydroxyl groups at both ends. Nearly all reactions to produce poly(silmethylenes) lead to end blocked polymers [3]. At first we had to solve two problems: a) synthesis of PDMSM with functional groups at both chain ends and b) exchange of these groups by hydroxyl groups. It is possible to divide the reactions of PDMSM synthesis described in the literature into two main groups (1) reactions of the GRIGNARD-type or on a similar basis, (2) ring-opening reaction of 1,1,3,3-tetramethyl-1,3-disilacyclobutane by a platinum catalyst.

In all cases it is necessary to start from chloromethyl dimethylchlorosilane (CMDMCS). This monomer CMDMCS was prepared by chlorination of trimethylchlorosilane [4,5]. The reaction



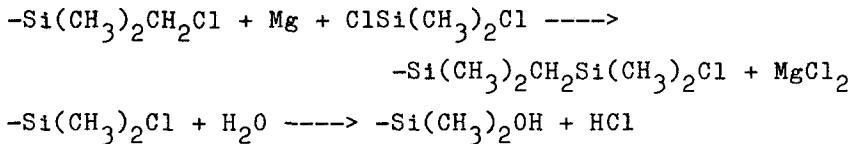
yields ca. 50 % CMDMCS [6]. Other products are unreacted trimethylchlorosilane and higher chlorinated chlorosilanes (tab. 1).

Table 1: Yields of chlorination of trimethylchlorosilane

	$\frac{\text{Kp}}{\text{°C}}$	yield	
		% [4]	% [6]
$(\text{CH}_3)_3\text{SiCl}$	55	18.9	20.8
$\text{CH}_2\text{ClSi}(\text{CH}_3)_2\text{Cl}$	113-115	45.5	49.9
higher chlorinated products	>120	35.7	29.3

Using highly pure monomers, it is possible to polymerize the CMDMCS to polymers of high molecular masses in the absence of moisture. The GRIGNARD reaction provides us with a polymeric PDMSM with a halogen group and an alkylmagnesium group which can be exchanged by a halogen group by reaction with dimethyldichlorosilane (scheme 1). The chain length of the poly(silmethylenes) is a function of the reaction time and the chloromethyl monochlorosilane/dichlorosilane ratio. In such a way it is possible to synthesize oligomeric as

well as high-polymeric products. Fig. 1 shows the conversion of CMDMCS to α,ω -dihydroxy poly(dimethyl silmethylenes) as a function of reaction time. In the scheme 1 of the GRIGNARD reaction of CMDMCS with magnesium, different reactions are possible to produce polymeric compounds. The linear PDMSM should have the same hydroxyl end groups at both chain ends. Therefore the following reactions are necessary:



The exchange of the α,ω -chloro groups takes place hydrolytically without damaging the silicon-carbon bond. Infrared and nuclear magnetic resonance spectra show the structure of the PDMSM formed (fig. 2). The characteristic absorption bands of the silicon-methylene-silicon groups are 1040 and 1350 $1/\text{cm}$ which we found in the respective samples.

Each polymer was tetrafunctionally end linked with a stoichiometrically equivalent amount of tetraorthosilicate using stannous(2-ethyl hexanoate) as a catalyst. The end-linking reaction gives polymeric networks at room temperature in a period of a few days. The functionality of the network junctions is 4. The determined parameters of the polymers and their networks are contained in the tab. 2. The molecular masses range from 7,000 to 25,000 g/mol, measured by end group analysis and gel permeation chromatography.

Investigations of networks

A sol gel analysis was carried out. The values of sol fraction thus obtained are given in tab. 2. The sol fraction contains the proportion of cyclic silmethylenes which are formed in the polymer building reaction. The amounts of soluble materials from 6 to 12 % are typical of this type of crosslinking reaction, and are in good agreement with published data. LEVIN and CARMICHAEL [7] observed less than 1 % low weight cyclic material.

The networks were investigated by classical methods of network characterization such as compression and stress-strain measurements. Fig. 3 shows the stress-strain isothermes for the end linked PDMSM networks in elongation in the unswollen state and compression in the swollen state, corrected to the unswollen state. The linearity of the curves at small elongations and compressions shows the correctness of measurements and demonstrates the ideal elastic behaviour of these networks. The same slope of the elongation and compression curves corresponds to the same molecular masses between the crosslinking points.

Table 2: Values of PDMSM polymers and its networks

	PDMSM-1	PDMSM-2	PDMSM-3	PDMSM-4	PDMSM-5
$M_n(\text{EG}), \text{g/mol}$	7,100	10,800	16,200	20,700	22,500
$M_n(\text{GPC}), \text{g/mol}$	7,200	11,000	20,300	25,000	26,200
w(sol), %	12.8	9.9	8.3	7.1	6.5
w(cyclic), %	7.0	5.1	4.3	4.1	3.7
$10^5, \text{mol/cm}^3$	11.81	8.30	5.24	4.21	4.01
A'	0.89	1.02	0.95	0.96	0.93
A	0.87	0.99	0.92	0.93	0.91
$2C_1$	0.255	0.197	0.128	0.102	0.095
$2C_2$	0.0064	0.0056	0.0035	0.0032	0.0022

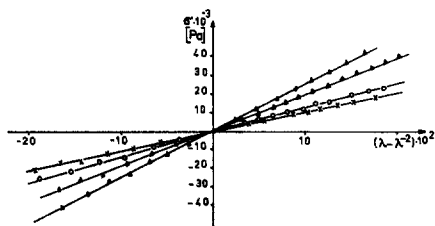


Fig. 3: Stress-strain curves of PDMSM networks of different mol. masses (tab.2) of the linear bifunctional polymeric chain at compression and elongation measurements. \blacktriangle PDMSM-1, \blacktriangle PDMSM-2 \circ PDMSM-3, \times PDMSM-4

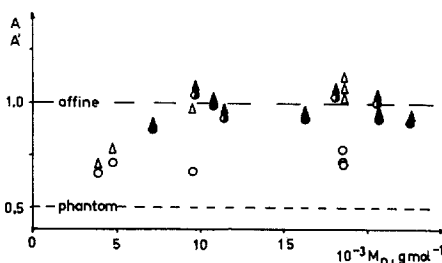


Fig. 4: Dependence of the structure factors A and A' on M_n for perfect end linked tetrafunctional networks. \circ , \triangle PDMSM, \bullet , \blacktriangle PDMSO [8], \circ , \triangle PDMSO [9].

Discussion of the results

Stress-strain data in elongation are mostly interpreted in terms of the reduced stress, defined by eq. 1

$$f^* = f / [(\lambda - \lambda^{-2}) A^*] ; \quad \bar{\sigma} = f / A^* \quad \text{eq. 1}$$

where f , λ and A^* represent the force, elongation ratio and cross-section area, respectively. The resulting values of f^* are plotted versus the reciprocal elongation as suggested by the semi-empirical equation of MOONEY and RIVLIN

$$f^* = 2C_1 + 2C_2 / \lambda \quad \text{eq. 2}$$

The constants C_1 and C_2 are independent of λ . The value of the modulus is $2C_1$ within the limit of large deformation; that is $1/\lambda \rightarrow 0$, and $2C_1 + 2C_2$ within the limit of small deformation ($1/\lambda \rightarrow 1$). In relation to the rubber elasticity theory the MOONEY-RIVLIN-constants correspond to eq. 3 within the limit of small deformation. At large deformations $2C_1$ corresponds to eq. 4.

$$2C_1 + 2C_2 = A'RT/(q_0^{2/3}M_n) \quad \text{eq. 3}$$

$$2C_1 = A RT/(q_0^{2/3}M_n) \quad \text{eq. 4}$$

The calculations of the factors A and A' were carried out. The values are listed in tab. 2. The structure factor A for a non-affine deformation of a ϕ -functional network is given by $1-2/\phi$, and should therefore be 1/2 for tetrafunctional networks. In the region of very small elongation the deformation should be nearly affine and the factor A' should be equal to unity for networks of any functionality. The present results are given in the table and show the affine deformation. The calculations yield A' = 0.96 with a standard deviation of 0.05. The observation that in this case A' and A are both equal to unity shows the affine deformation within the limit of small and large deformations. Fig. 4 illustrated the variety of published experimental results of A and A'. The structure factor A is plotted versus the molecular masses of polymers prior to their crosslinking. There are no data of poly(dimethyl silmethylene) networks in the literature. Therefore, in fig. 4, we find values of published results of PDMSO in comparison with PDMSM values. The full circles and triangles designate the PDMSM results. All of the values were observed in elongation measurements of unswollen samples prepared without solvents. The dashed lines mark the A values of affine and phantom deformations respectively. The PDMSM values of C_2 of the MOONEY-RIVLIN-equation are not in agreement with the results of PDMSO by MARK [9]. We found values which were much lower than those published. Fig. 5 shows the MOONEY-RIVLIN-constant $2C_1$ as a function of molecular mass of network chains. PDMSM and PDMSO results give the same dependence of $2C_1$ and M_n . Fig. 6 shows the $2C_2/2C_1$ ratio versus reciprocal molecular mass of network chains. Our values of $2C_2$ represent less than 10 % of the PDMSO values. It is a matter of fact that our measurements were carried out at small elongations. We can assume an ideal elastic behaviour of our prepared PDMSM networks.

The thermodynamic quantity f_e/f , the energetic contribution f_e to the elastic force f exhibited by a deformed polymer network is of primary interest. In the case of uniaxial deformation (elongation or compression) it is given by eq. 5, where U, l, T and V are the energy, length, absolute temperature and volume of the sample, respectively.

$$f_e = (\partial U / \partial l)_{T,V} \quad \text{eq. 5}$$

$$f_e/f = -T \left[\frac{\partial \ln(f/T)}{\partial T} \right]_{\lambda,p} + \beta T/3 \quad \text{eq. 6}$$

$$f_e/f = T \, d \ln \langle L^2 \rangle_0 / dT \quad \text{eq. 7}$$

The most useful form of representing such information is the fraction f_e/f which is of energetically intramolecular origin. This ratio is given for measurements at constant pressure and deformation by eq. 6, where β is the thermal expansion coefficient $[(1/V)(\partial V/\partial T)_p]$ of a polymer network. Assuming that in the deformation of a polymeric net-

Table 3: Thermoelastic results on PDMSM networks

f_e/f	$10^3 \, d \ln \langle L^2 \rangle_0 / dT \, (K^{-1})$
0.00 + 0.04	0.00 + 0.15
-0.20 ± 0.10 (a)	0.00 ± 0.10 (b)
0.21 ± 0.06 (e)	0.21 ± 0.15 (c)
	0.43 ± 0.11 (d)
	0.20 ± 0.20 (c)

(a) calculated from data of [2], (b) from viscosity measurements, (c) from direct thermoelastic measurements [2], (d) from stress-strain isothermes [2], (e) ref. [1]

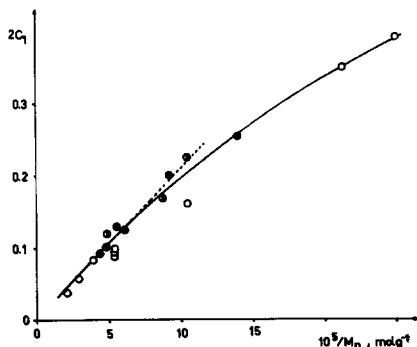


Fig. 5: Dependence of the MR-constant $2C_1$ on M_n , symbols see fig. 4

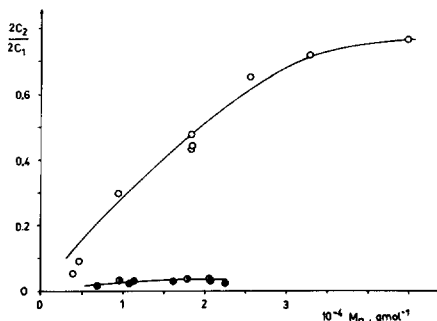


Fig. 6: Dependence of the ratio $2C_2/2C_1$ on M_n , symbols see fig. 4

work any energy change is intramolecular in origin, a molecular interpretation of thermoelastic data is possible by eq.7,

where $\langle L^2 \rangle_0$ represents the unperturbed dimensions of the

network chains. It permits the comparison of thermoelastic measurements of network chains with results of viscosity measurements of isolated chains and results of the rotational isomeric state theory of chain configuration. Table 3 shows our calculated ratio of energetic force to total force of the synthesized and measured poly(dimethyl silmethylene) networks. Our value $f_e/f = 0.00 \pm 0.04$ is near zero. The value of $d \ln \langle L^2 \rangle_0 / dT = (0.00 \pm 0.10) 10^{-3} K^{-1}$ is in good agreement with results of viscosity measurements [2]. The values of f_e/f and $d \ln \langle L^2 \rangle_0 / dT$ are smaller than those of PDMSO [3].

It is evident that the polymeric chain of PDMSM contains a very small fraction of energetic force by elastic deformation. The main part of the elastic force is only of an entropical nature.

References

1. Llorente, M.A., Mark, J.E., Saiz, E., J. Polym. Sci. Polym. Phys. Ed. 21, 1173 (1983)
2. Ko, J.H., Mark, J.E., Macromolecules 8, 869 (1975)
3. Schimmel, K.H., Wiss. Zeitschr. TH Merseburg, in prep.
4. Krieble, R.H., Elliott, J.R., J. Amer. Chem. Soc. 67, 1810 (1945)
5. Speier, J.L., J. Amer. Chem. Soc. 73, 824 (1951)
6. Pham the Trinh, Dissertation A Merseburg 1987
7. Levin, G. Carmichael, J.B., J. Polym. Sci. A1 6, 1 (1968)
8. Schimmel, K.H., Pham the Trinh, 31st IUPAC Macromol. Symp. Macro'87, Merseburg, GDR, 1987
9. Queslel, J.P., Mark, J.E., Adv. Polym. Sci. 65, 135 (1984)