

Some Investigations on Structure and Physical Properties of Poly-(Dimethyl-Siloxane) and Poly-(Methyl-Phenyl-Siloxane) Model-Networks

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Summary

Networks were prepared from Poly-(Dimethyl-Siloxane), PDMS, and Poly-(Methyl-Phenyl-Siloxane), PMPS, precursor chains by telechelic condensation. The precursor was of a very low polydispersity. The functionality of the crosslinks was four.

Thermomechanic, calorimetric, and swelling experiments were carried out to characterize the resulting rubbers. Generally the results show a good agreement with theory in the case of PDMS.

Introduction

Linear Poly-(Siloxane) chains with strictly α , β -functionality are easy to synthesize. So they are a very attractive basis material for the attempt to build up "tailor made" networks. "Tailor made" means that chainlength distribution is very narrow, the functionality of the crosslinks is well defined, and that the crosslinking process is possible at fixed and well-known parts of the chain solely (1).

Networks prepared under these aspects might be a further step towards the construction of a network with predictable qualities (1).

The crosslinking reaction is the step in the whole synthesis, where defects are woven into the regularity of the network. These may be loops, free chainends, vacant functionalities, etc..

The synthesized networks are therefore not ideal ones but notwithstanding they exhibit some model character in contrast to usual ones.

The customary techniques to prepare α , β -functional siloxanes leads to polymers of high polydispersity $P = M_w/M_n$ with values of $P = 2 \dots 3$ (2).

In this work the method published by Lee and Johannsen (4) was employed to synthesize PDMS α , β -diol with $P = 1.10$ and $M_w = 13.200$ g/mol and PMPS α , β -diol with $P = 1.27$ and $M_w = 5.400$ g/mol.

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Networks from these precursor chains were investigated by free swelling and swelling pressure measurements, thermo-mechanic analyser and torsional pendulum. This to obtain the molar mass of the elastic chains from the macroscopic behaviour of the network to compare these values with those of the precursor chains.

The results give some hints on the crosslinking reaction of PDMS with those carried out with PMPS with its more voluminous phenyl-substituent. The results concerning the temperature range of glass- and melting transition obtained from measurements of the temperature dependence of the moduli G' (storage modulus) and G'' (loss modulus) are confirmed by calorimetric experiments.

Detailed data could be obtained from these systems concerning the behaviour of the G' -modulus in the rubber elastic state.

Materials and methods

Hexamethylcyclotrisiloxane (D_3), Octamethylcyclotetrasiloxane (D_4)

The cyclic dimethylsiloxanes were prepared and purified by convenient methods (30).

Methyl-Phenyl-Cyclotrisiloxane (MP)₃, Methyl-Phenyl-Cyclotetrasiloxane (MP)₄

The cyclic Methyl-Phenyl-Siloxanes were prepared and purified by convenient methods (30).

Anionic Polymerization

The anionic polymerization was carried out with both the cyclic products D_3 and cis - $(MP)_3$ according to the procedure described by Lee and Johansson (4) with Benzyltrimethylammonium-bis(o-Phenylenedioxi)Phenylsiliconate as catalyst in Toluene in the presence of DMSO at 50 °C.

The reaction was controlled by gelpermeation chromatography (GPC).

The polymers had to be freed from unreacted cycles. This was done by extraction or precipitation respectively.

Preparation of the rubber

The anionic polycondensation yields α , ω - terminated polymer chains which were crosslinked at roomtemperature with an orthosilicate in the presence of a catalyst.

Gelpermeation Chromatography

The analyses were carried out with a complete set of six Waters μ -Styragel columns.

The characterization was achieved according to Benoit et al. (8, 9).

Swelling Experiments

Measurements of swelling pressure were done according to the method described by Borchard et al (10).

Calorimetric measurements

They were carried out with the DSC-2 system from Perkin-Elmer. If not otherwise quoted, the cooling-rate was 80°/min and the heating-rate was 20°/min.

Thermomechanic analysis

These measurements were carried out with the Perkin-Elmer TMS-2 system according to the method described by HWO et al (26).

Torsional-pendulum measurements

These measurements were carried out with an automatically controlled torsional-pendulum system by Fa. Myrenne D-4170 Roetgen, FRG, a modified system of Illers and Breuer (11) and (12, 13).

These experiments were run at a frequency of $1 \pm 0,1$ Hz in temperature steps up to 5° taking 5 min for each value. Cooling-rate was 3°/min.

Theoretical

Dynamic-mechanic torsion

For PDMS and PMPS $G' \gg G''$ is generally valid at a frequency of 1 Hz.

The frequency dependence of the G' -modulus may be neglected (14, 15). This means that the dynamic torsional modulus may be taken as the equilibrium modulus in this special case, so that relationship of rubberelastic theory are valid.

According to (19) the equilibrium modulus G is related to the molar mass M_C of the elastic chain of a rubber:

$$|G| = A \phi \rho_{02} \frac{RT}{M_C} \quad (1)$$

$$|G| = |G' + iG''| \quad (2)$$

and the condition $G' \gg G''$ leads to $G' \approx G$ provided the rubber is unstrained and unswollen.

G = complex equilibrium modulus of torsion; $i = \sqrt{-1}$
 G' = storage modulus; G'' = loss modulus; ϕ = front factor (16) respectively memory term (17); ρ_{02} = density of the dry network;
 M_C = molar mass of the elastic chain; M_n = number average of the molar mass; M_w = weight average of the molar mass; R = gas constant, T = thermodynamic temperature; A is a constant factor with the value $A = 1-f/2$, f being the functionality of the crosslink, in this case $A = 1/2$ (19 - 24). M_C is a number average, so that in an ideal network M_C is expected to be

identical with M_n of the precursor (18).

Thermomechanic analysis

From the elastic theory one obtains in the case of an uniaxial deformation of a volume element:

$$\frac{F_z}{l_0} = A \cdot \phi \rho_0 \frac{RT}{M_c} \left(\lambda - \frac{1}{\lambda^2} \right) \quad (3)$$

or with eq. 1:

$$\frac{F_z}{l_0} = G \left(\lambda - \frac{1}{\lambda^2} \right) \quad (4)$$

Eq. 4 gives another instruction to obtain the G modulus, in this case from thermomechanic analysis.

F_z = force in z-direction; l_0 = length in the unstrained state;

l = length in the strained state.

The internal energy contribution f_e to the equilibrium stress f is given according to (26):

$$\frac{f_e}{f} = 1 - \frac{T}{G} \frac{dG}{dT} - \frac{1}{3} \beta_v T \quad (5)$$

β_v = cubic thermal expansion coefficient of the sample;

λ is equal to l/l_0

Swelling experiments

If a polymer network is exposed to a low-molecular solvent swelling occurs and the following equations are valid in equilibrium:

$$\Delta\mu_1 = \mu_1 - \mu_{O1} = RT \left[\ln(1-v) + v + \chi v^2 + (\bar{V}_{O1} \rho_{O2} / M_c) (A v^{\frac{1}{3}} \phi - B v) \right] \quad (6)$$

In the case of free swelling experiments:

$$\Delta\mu_1 = \mu_1 - \mu_{O1} = 0 \quad (7)$$

In the case of swelling pressure experiments:

$$\Delta\mu_1 = \mu_1 - \mu_{O1} = - \Pi_Q V_{O1} \quad (8)$$

μ_{O1} = chemical potential of the pure solvent;

μ_1 = chemical potential of the swollen gel in equilibrium;

v = polymer concentration by volume; χ = solvent-polymer interaction parameter, depending on concentration, pressure, temperature but little on the functionality of the crosslinks; \bar{V}_{O1} = molar volume of the pure solvent; B is a constant in this case assumed to be $B = 0$ (19 - 24);

Π_Q = swelling pressure.

The result of the experiments may be evaluated according to the methods of Mula and Chinellato (25) or by combining free swelling and swelling pressure measurements.

Both methods yield χ and M_c .

Results and discussion

The numerical results are listed in the following tables and figures:

T=25°C	Precursor	
	GPC	
	$\frac{M_w}{g.mol^{-1}}$	$\frac{M_n}{g.mol^{-1}}$
PDMS	13.200	12.000
PMPS	5.400	4.200

Table 1: The precursor chains

Table 2: The network; ^{+) Free swelling experiments; χ obtained from interpretation according to (25). All investigations on the plots cited in (25) led to the same χ - value}

Network						
swelling ⁺⁾	swelling pressure (25)		TMA (26)		Pendulum	
$\frac{M_c}{g.mol^{-1}}$	$\chi_{25\text{ }^\circ\text{C Toluene}}$	$\frac{M_c}{g.mol^{-1}}$	$\frac{M_c}{g.mol^{-1}}$	A.φ	$\frac{M_c}{g.mol^{-1}}$	
PDMS 13.000	0,53	9.700	9.500	1,04	9.800	
PMPS 12.100	0,64	11.900	14.700	1,19	8.900	

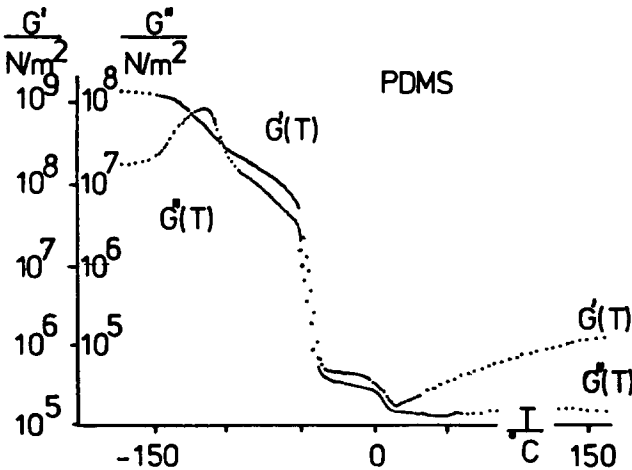


Figure 1: Diagram from torsional pendulum experiment. Rubber from PDMS with $M_w = 13.200$ g/mol

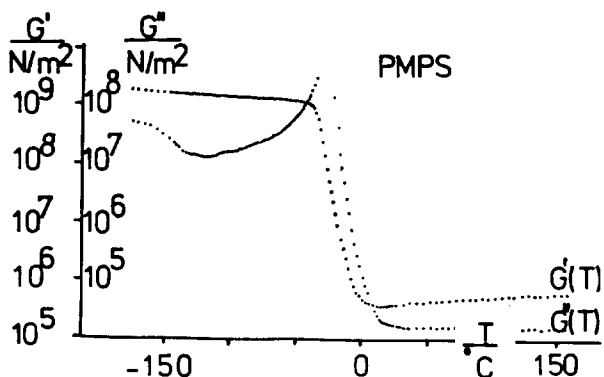


Figure 2: Diagram from torsional pendulum experiment.
Rubber from PMPS with $M_w = 5.400$ g/mol

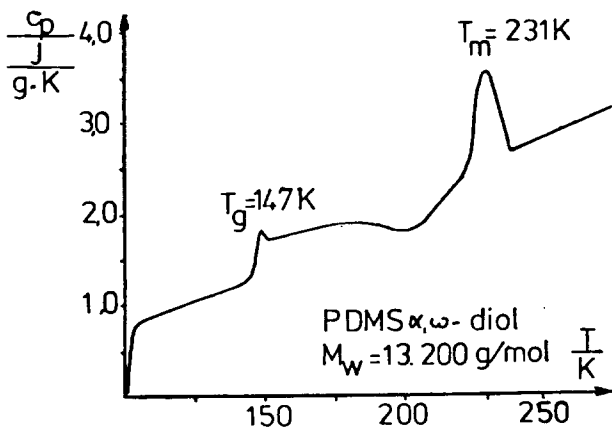


Figure 3: DSC diagram of the precursor chain

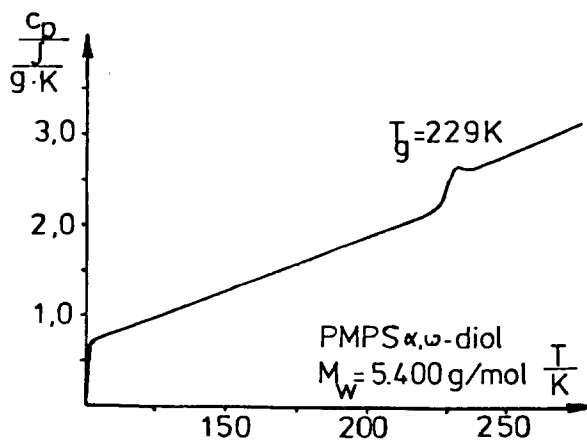


Figure 4: DSC diagram of the precursor chain

Concerning the interpretation of the swelling pressure experiments one has to put emphasis to the fact that the evaluations from the plots proposed by Mula and Chinellato (25) are not very exact with respect to M_C . M_C has to be calculated from the intercept of a linearized equation. Relative small variations in the value of the intercept lead to strong variations of the evaluated M_C . Thus M_C can only be calculated in the order of magnitude.

Nevertheless the evaluation of the χ -parameter leads to values with reasonable reliability.

The swelling pressure measurements therefore should be accompanied by a free swelling experiment. In our experiments the error was estimated to be about 18 %.

For PDMS the results of swelling experiments are in good agreement with dynamic-mechanical respectively the thermomechanical experiments. The errors were calculated to be about 10 % and 12 % respectively. Furthermore one has to take into account that the G-modulus is much more sensitive to network defects than swelling experiments are (1, 27). The values of M_C estimated via G-modulus were found to be lower than M_n of the precursor.

At low degrees of swelling e. g. at high values of swelling pressure better agreement of the results from swelling and mechanical measurements were found. This leads to the assumption that this effect may be due to a non-gaussian distribution of the chains in the high swollen polymer system. In general the results concerning PDMS are in good agree with the findings of Mark (28) and of Mark and Sullivan (3) which were carried out with PDMS of a higher M_w/M_n ratio. The rubber contained 1,6 % (w/w) extractable material, which was mainly low molecular material and catalyst.

On the contrary PMPS shows greater differences between M_n of the precursor and M_C calculated from the network properties. There was much more extractable material found in this rubber - about 30 % (w/w) - containing polymer material.

The M_C values are significantly higher than expected from the M_n values of the precursor.

Steric hindrance may be due to this and via conformationary effects also cause the high energetic contribution to the total elastic force. Figure 1 and 2 show the course of the $G'(T)$ and the $G''(T)$ moduli for PDMS respectively PMPS networks under investigation. Figure 3 and 4 represent the differential calorimeter diagram of the uncrosslinked polymers.

In the case of PDMS both precursor and network show glass transition and melting processes. PMPS on the contrary did only show a glass transition within the investigated temperature range. X-ray diffractometric experiments did not exhibit signals due to crystalline regions.

In the rubber elastic state both rubbers exhibit the increase of the G' modulus with temperature as claimed by theory.

Figure 5 shows the corresponding diagram. For PDMS the ratio G'/T seems to be approximately constant from 20 °C to 100 °C. For PMPS the ratio decreases with increasing temperature.

A constant ratio G'/T is predicted from theory for a merely entropy elastic rubber (29).

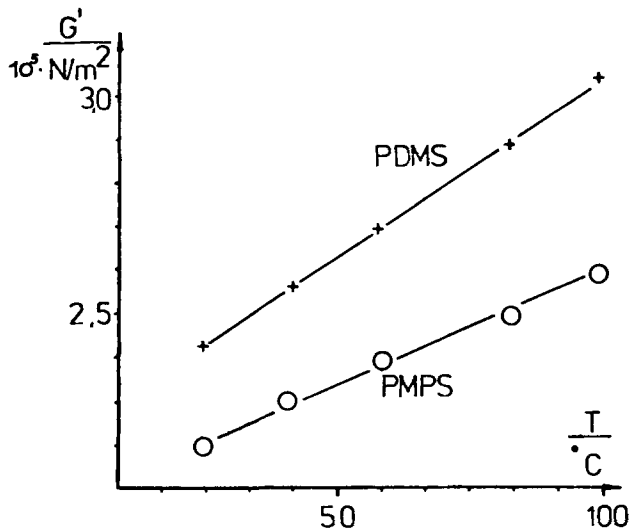


Figure 5: Graph of the function $G'(T)$ for PDMS and PMPS taken from the results of the thermomechanical investigations of the networks.

Both samples exhibit a modulus increasing with temperature. Only PDMS shows a nearly constant ratio $G'(T)/T$.

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