

Interpenetrating polymer networks of poly(dimethylsiloxane): 1. Preparation and characterization

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Model networks of α,ω -dihydroxy-poly(dimethylsiloxane) (PDMS) were prepared by tetrafunctional crosslinking agent tetraethyl orthosilicate (TEOS) and the catalyst stannous 2-ethylhexanoate. Hydroxyl-terminated chains of PDMS having molecular weights 15×10^3 and $75 \times 10^3 \text{ g mol}^{-1}$ were used in the crosslinking reaction. Bimodal networks were obtained from a 50% (w/w) mixture of PDMS chains with $M_n = 15 \times 10^3$ and $75 \times 10^3 \text{ g mol}^{-1}$. A sequential interpenetrating network of these PDMS chains was also prepared. Physical properties of the elastomers were determined by stress-strain tests, swelling and extraction experiments, and differential scanning calorimetry measurements.

(Keywords: poly(dimethylsiloxane); interpenetrating networks; physical properties)

INTRODUCTION

The properties of 'model' or 'ideal', tailor-made networks have been studied extensively during the past decade. The model network is a network in which the chains have the same average length and distribution of lengths as the non-crosslinked chains from which it was prepared. Preparation of these elastomeric networks by endlinking polymers with reactive chain ends permits a direct and independent measure of average chain-length distribution. A precise control of the network chain-length distribution is very important for better understanding of rubber elasticity¹.

Poly(dimethylsiloxane) (PDMS) has the advantage of thermal stability and very low melting temperature (-40°C). PDMS networks can be prepared using a multifunctional crosslinking agent such as tetraethyl orthosilicate (TEOS)².

Unimodal networks of PDMS are prepared from only one kind of prepolymer with a known chain length; if more than one type of chain is used in network formation, these are called bimodal or interconnected chains. Generally, bimodal PDMS networks consisting of very short chains and relatively long chains are studied because of the improvements in mechanical properties they provide³.

Although PDMS and its networks show several interesting properties, such as high permeability to many gases and biocompatibility, their mechanical properties are rather poor. Inorganic fillers like silica are used to reinforce these materials⁴.

Introducing glassy polymers into silicon or preparation of interpenetrating networks (IPNs) of PDMS provide alternative approaches to improve mechanical properties⁵⁻⁸. IPNs are combinations of crosslinked polymers held together by permanent entanglements. Simultaneous

and sequential formation of IPNs are the main methods for preparation of these type of networks^{9,10}.

The present study concerns the preparation and characterization of unimodal, bimodal and sequential interpenetrating networks of PDMS and comparison of their mechanical and elastomeric properties.

To report the results of semi- and full IPNs of PDMS and various vinyl and diene polymers will be the subject of the second paper in this series.

EXPERIMENTAL

Materials

Linear α,ω -dihydroxy-poly(dimethylsiloxane)s (PDMS) were products of Wacker-Chemie GmbH, München. They were dried at 70°C in a vacuum oven for 24 h. Two prepolymers, PDMS-15 and PDMS-75, having number-average molecular weight 15×10^3 and $75 \times 10^3 \text{ g mol}^{-1}$, respectively, were used in this work.

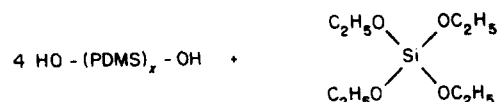
Tetraethyl orthosilicate (TEOS) was a product of Fluka AG and was used as a crosslinking agent. Its purity was better than 98% and it was used without purification.

Stannous 2-ethylhexanoate was a product of Sigma Chemical Co. and was used as catalyst for the polycondensation reaction.

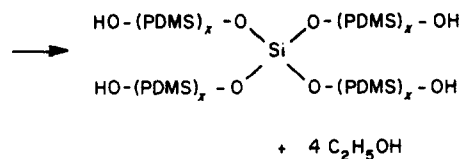
Benzene, tetrahydrofuran, toluene and methanol were products of Merck AG. These were used as solvents in extraction and swelling experiments without any purification.

Procedure

Preparation of PDMS elastomers. Elastomers of PDMS were prepared using the following reaction¹:



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(1) First, 5 g of PDMS-15 prepolymer was mixed with TEOS (crosslinking agent) and stannous 2-ethylhexanoate (catalyst); TEOS was used in stoichiometric amount and stannous 2-ethylhexanoate was added in an amount of 0.3–0.5 wt% to the mixture. The mixture was poured into a Teflon-coated aluminium mould with interior dimensions $9 \times 4 \times 0.15 \text{ cm}^3$. The reaction was carried out in a vacuum oven at room temperature. After 24 h the network was turned over for better removal of ethanol, which was a by-product of the polycondensation reaction given above. This crosslinking reaction was continued for 48 h in all.

(2) The prepolymer, PDMS-75, was crosslinked by using a similar procedure to that described above. However, owing to the high viscosity of the prepolymer, mixing of reagents was carried out with difficulty. Therefore, PDMS-75 was first dissolved in benzene; TEOS and the catalyst were subsequently added into this solution. The reaction mixture was poured into a deeper mould of $9 \times 4 \times 1.5 \text{ cm}^3$ dimensions. Then, benzene was allowed to evaporate before applying vacuum in order to prevent the formation of defects in the film.

(3) The prepolymers, PDMS-15 and PDMS-75, were mixed in 50% (w/w) ratio to obtain a bimodal network. The same reaction procedure described in (1) was applied.

Preparation of interpenetrating network. PDMS-75 crosslinked elastomer was prepared according to the procedure above. It was then swollen in the mixture of linear prepolymer of PDMS-15, a stoichiometric amount of its endlinking agent TEOS and 0.3–0.5 wt% stannous 2-ethylhexanoate catalyst for 12 h. The crosslinking reaction for linear PDMS-15 was carried out under vacuum for 48 h as described above. The PDMS-15 content in the IPN sample formed was 28%.

Characterization of elastomers. Characterization of networks was made with the following physical methods: extraction of uncrosslinked material, swelling experiments of networks, stress-strain tests and differential scanning calorimetry.

Extractions of the networks resulted in the removal of soluble, linear material. Samples of each network were kept in tetrahydrofuran, and later in toluene for periods of 3 days at room temperature, and networks were

deswollen in toluene-methanol mixture. The extracted samples were dried under vacuum and soluble fractions of the networks were calculated.

Swelling experiments were performed to determine the crosslink density and M_c (the average chain length between junctions) for each network. Swelling measurements were carried out in benzene at room temperature. Volume fraction of polymer at equilibrium (at maximum swelling) was determined by gravimetry. The weighed strips of each network were kept in benzene until equilibrium was attained, then weights of swollen samples were determined. Volume fraction of polymer, v_{2m} , was calculated by assuming additivity of volumes. Another method to calculate v_{2m} was to measure the dry and swollen lengths of the samples by Gaertner cathetometer. The average values of v_{2m} calculated by the two methods were reported.

Mechanical properties of the networks were also studied. The tensile strength and elongation measurements were performed on a Tensilon (UTMII) tester at room temperature with a crosshead speed of 5 mm min^{-1} . Young's modulus E , tensile strength f_u and ultimate elongation or elongation at break were determined. The results reported are the average of four specimens.

Differential scanning calorimetry (d.s.c.) measurements were conducted in a Shimadzu DSC-41 apparatus at a heating rate of $10^\circ\text{C min}^{-1}$. After obtaining a uniform thermal history, reproducible scans were recorded and glass transition temperature was taken at the onset of the corresponding heat-capacity jump. The melting temperature was reported at the minimum of the endothermic peak.

RESULTS AND DISCUSSION

Extraction and swelling properties

The results of extraction and swelling measurements of PDMS elastomers are given in Table 1. The uncrosslinked linear part of each network is calculated by using extraction results. Volume fractions v_{2m} at equilibrium swelling and swelling ratios Q ($1/v_m$) were evaluated for crosslinked portions of each network. The volume fraction of PDMS elastomer decreases as the molecular weight of the prepolymers increases; longer chains have higher swelling ratio.

The molecular weight between junctions of the prepared networks is calculated by using the following Flory-Rehner equation^{1,4,11,12}:

$$M_c = \frac{-c\rho V_1(v_{2m}^{1/3} - v_{2m})}{\ln(1 - v_{2m}) + \chi v_{2m}^2 + v_{2m}} \quad (1)$$

Table 1 Extraction and swelling equilibrium measurements of PDMS elastomers

Sample designation	M_n ($10^{-3} \text{ g mol}^{-1}$)	Linear parts (%)	v_{2m}	Q	$\chi^{(a)}$	$\chi^{(b)}$	$M_c^{(c)}$	$M_c^{(d)}$
PDMS-15	15	5.2	0.262	3.82	0.566	0.583	14.9	15.4
PDMS-75	75	17.9	0.129	7.75	0.519	0.518	78.9	76.3
Bimodal network	25	12.4	0.167	5.98	0.532	0.537	22.2	26.5
Sequential IPN	–	13.1	0.165	6.06	–	–	–	–

^a Interaction parameter calculated using Brotzman and Eichinger's work^{13,14}

^b Interaction parameter evaluated from the data of Newing, Summers and Tewari^{16,17}

^c The average chain length between junctions calculated by using $\chi^{(a)}$

^d The average chain length between junctions calculated by using $\chi^{(b)}$

In the above equation, M_c is the number-average molecular weight of the chains between junctions, V_1 is the molar volume of benzene at room temperature ($89.08 \text{ cm}^3 \text{ mol}^{-1}$), ρ is the density of the PDMS network, χ is the interaction parameter between polymer and solvent, c is a constant (equal to $1/2$ for the network of phantom chains and 1 for the affine network assumption) and w is a parameter that takes into account a possible volume-dependent contribution to the free energy of network deformation. For a tetrafunctionally crosslinked network the value of w is between 0 and $1/2$.

The value of M_c is a parameter used to characterize the polymer network. M_c values evaluated from swelling measurements through the application of Flory–Rehner equation are given in Table 1. For these calculations, the χ parameter was determined in two different ways. The first is from Brotzman and Eichinger's work¹³ using Shih and Flory's data¹⁴ for PDMS in benzene at 25°C , as given below:

$$\chi = 0.477 + 0.315v_2 \quad (2)$$

where v_2 is the uncrosslinked polymer volume fraction, which is evaluated through the following fourth-degree polynomial¹³:

$$\Delta v = 0.0173v_{2m} + 0.0978v_{2m}^2 + 0.5394v_{2m}^3 + 0.1161v_{2m}^4 \quad (3)$$

where Δv is the difference between volume fractions of uncrosslinked and crosslinked networks. It is known that M_c values are very sensitive to interaction parameter, χ . Therefore, another approach is also used to calculate χ of a PDMS network in benzene at room temperature.

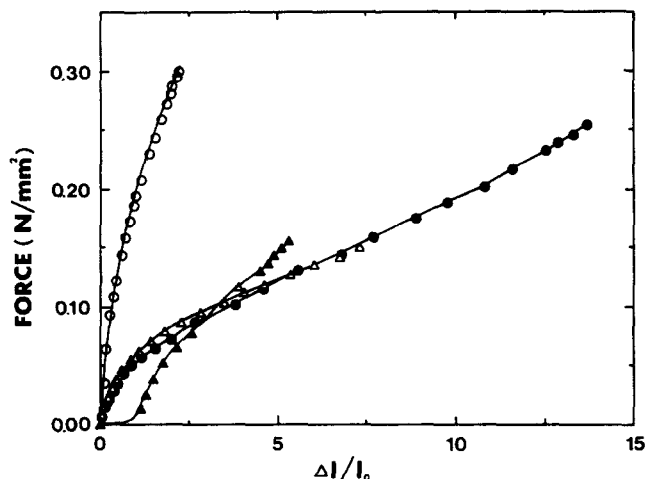


Figure 1 Stress-strain curve for PDMS elastomers: (○) PDMS-15 network; (●) PDMS-75 network; (△) sequential full IPN; (▲) bimodal network

For this purpose the data of χ and v_{2m} given in ref. 15 by Newing¹⁶ and Summers¹⁷ were plotted and χ of PDMS was determined. It will be seen from Table 1 that χ ($\chi^{(a)}$ and $\chi^{(b)}$) parameters calculated by using the above-mentioned two procedures are in quite reasonable agreement.

In the application of the Flory–Rehner relation^{11,12}, c and w values are two constants that also affect the calculation of M_c values (equation (1)). For PDMS-15 and PDMS-75 networks, $M_c^{(c)}$ values calculated by using $\chi^{(a)}$, $c=1$, $w=1/2$ are in agreement with the chain length of original prepolymers, which means both networks fit the affine network assumption, and hence there are no fluctuations for crosslinks about their mean positions. However, for the PDMS-15 network, since $\chi^{(b)}$ is considerably different $\chi^{(a)}$, it is necessary to use $c=1/2$ and $w=1/2$ in equation (1), in order to obtain the reported result in Table 1. On the other hand, in the case of the network that was prepared by mixing PDMS-15 and PDMS-75 linear prepolymers in 50 wt% ratio, a phantom-chain behaviour with constants $c=1/2$, $w=1/2$ for both interaction parameters, $\chi^{(a)}$ and $\chi^{(b)}$, is exhibited.

Mechanical properties

Figure 1 illustrates the stress–strain curves for PDMS elastomers. Evaluated parameters for the above-mentioned four samples are given in Table 2. It will be seen that PDMS-75 has quite high ultimate elongation (1371%) although it has relatively low tensile strength at break and Young's modulus when compared with PDMS-15. The network prepared from the mixture of linear PDMS-15 and PDMS-75 shows an ultimate elongation value (477%) that is between the two values obtained for the networks of PDMS-15 and PDMS-75. However, it is not easy to explain the lower tensile strength and modulus of this sample with respect to PDMS-75. Sequential interpenetrating networks of PDMS-75 and PDMS-15 exhibit a decrease in ultimate elongation, tensile strength and modulus relative to pure PDMS-75 network.

Another approach to evaluate M_c value or molecular weight of the chain sections in the network is determination of modulus from stress–strain measurements. The elongation behaviour of the dry test specimen was described by the following equation^{18,19}:

$$\sigma = \frac{\rho RT}{M_c} (\lambda - \lambda^{-2}) = C_0 (\lambda - \lambda^{-2}) \quad (4)$$

where σ is the tensile stress, R is the gas constant, T is the absolute temperature, λ is the deformation ratio ($\lambda = l/l_0$, l and l_0 represent the length of elongated and original samples, respectively), ρ is the density of polymer and M_c is the number-average molecular weight of the

Table 2 Results of mechanical experiments of PDMS elastomers

Sample	M_n ($10^{-3} \text{ g mol}^{-1}$)	Ultimate elongation (%)	f_u (N mm^{-2})	E (N mm^{-2})	M_c ($10^{-3} \text{ g mol}^{-1}$)
PDMS-15	15	222	0.300	0.1351	17.7
PDMS-75	75	1371	0.253	0.088	80.3
Bimodal network	25	477	0.156	0.033	35.4
Sequential full IPN	–	728	0.150	0.082	87.9

chain between two junction points. From the elastic, namely linear, part of the stress-strain curve, the Young's modulus $E (=3C_0)$ was determined and M_c values were evaluated and given in Table 2.

The stress-strain data were also evaluated by using the 'reduced stress' equation as follows:

$$f^* = \frac{f}{A^*} (\lambda - \lambda^{-2}) \quad (5)$$

where f^* is the reduced stress (N mm^{-2}), f is the equilibrium force (N), A^* is the cross-sectional area of each network sample in the unstretched state and λ is the elongation or relative length of the network.

The experimental data in simple tension are presented in Figure 2 in terms of the following familiar Mooney-Rivlin expression²⁰:

$$f^* = 2C_1 + 2C_2 \lambda^{-1} \quad (6)$$

where $2C_1$ is the elasticity modulus at very high elongations ($\lambda^{-1}=0$) and $2C_2$ is the slope of the line in the plot of f^* vs. λ^{-1} (l_0/l).

The results of reduced stress as a function of reciprocal elongation are depicted in Figure 2. M_c values of the network chains can be obtained by using the following expression⁴:

$$(f^*)_{ph} = \frac{(1 - 2/\Phi)\rho RT}{M_c} \quad (7)$$

In the above relation $(f^*)_{ph}$ is the shear modulus of the phantom network (N mm^{-2}) and $\Phi (=4)$ represents the average functionality of the junctions in our network. $(f^*)_{ph}$ is identical to $2C_1$ in equation (6) and can be

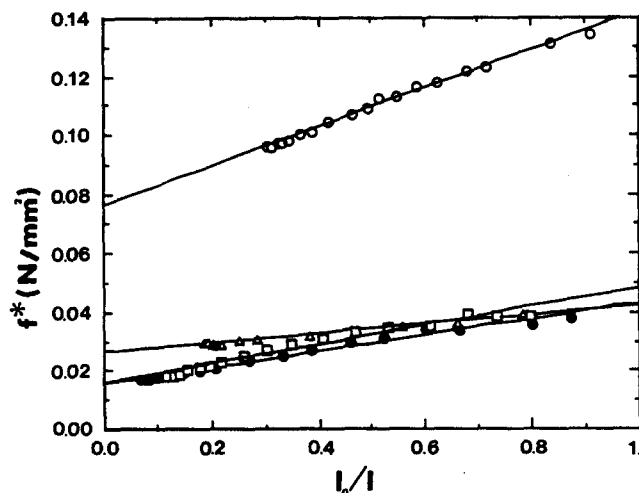


Figure 2 Reduced stress shown as a function of reciprocal elongation for PDMS networks: (○) PDMS-15 network; (●) PDMS-75 network; (□) sequential full IPN; (△) bimodal network

obtained from Figure 2. Experimental $2C_1$ and $2C_2$ values of networks are given in Table 3.

Theoretical values of $(f^*)_{th}$ calculated from equation (7) by using M_n values of the networks are included in Table 3. The experimental $2C_1$, calculated $(f^*)_{th}$ as well as M_c values are in good agreement for PDMS-15 and PDMS-75 networks. However, in the case of the bimodal network, there is a deviation between experimental and calculated values of the above parameters.

Sequential full IPN samples show similar behaviour to the PDMS-75 sample. Its experimental $2C_1$ value is relatively larger than that of the PDMS-75 network; however, it does not change its M_c value too much.

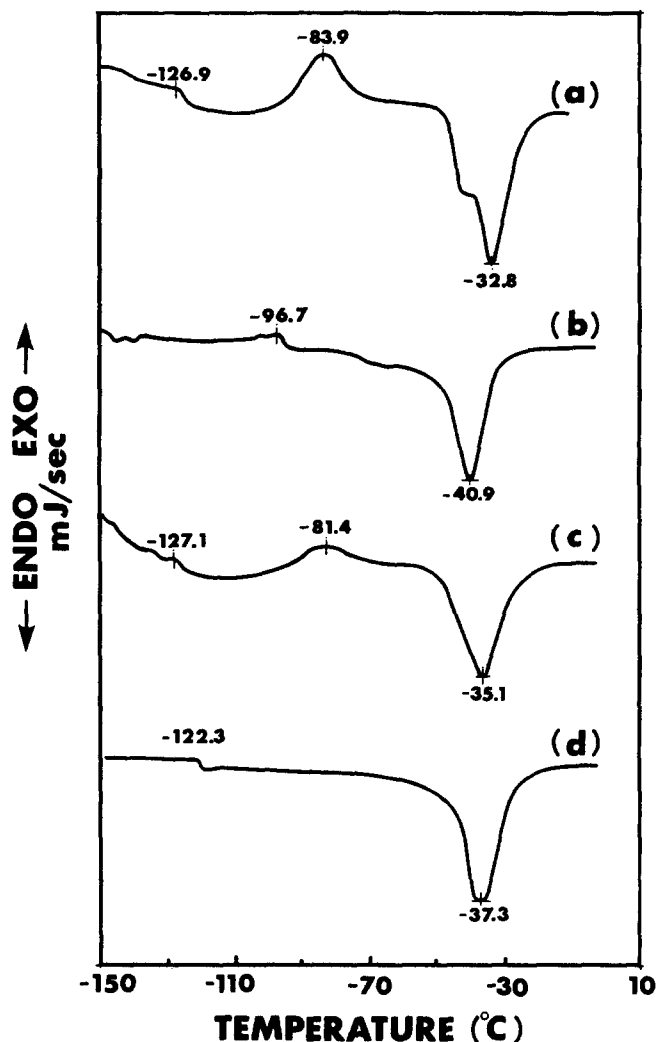


Figure 3 D.s.c. thermograms of PDMS prepolymers and networks: (a) linear PDMS-15 prepolymer; (b) crosslinked PDMS-15 network; (c) linear PDMS-75 prepolymer; (d) crosslinked PDMS-75 network

Table 3 Elasticity constants and reduced stress values for PDMS networks

Sample designation	M_n ($10^{-3} \text{ g mol}^{-1}$)	$2C_1$	$2C_2$	M_c ($10^{-3} \text{ g mol}^{-1}$)	$2C_2/2C_1$	f^*_{th}
PDMS-15	15	0.0760	0.0662	15.5	0.869	0.0798
PDMS-75	75	0.0154	0.0277	76.5	1.800	0.0157
Bimodal network	25	0.0260	0.0160	45.1	0.062	0.0467
Sequential full IPN	-	0.0158	0.0326	76.0	2.063	-

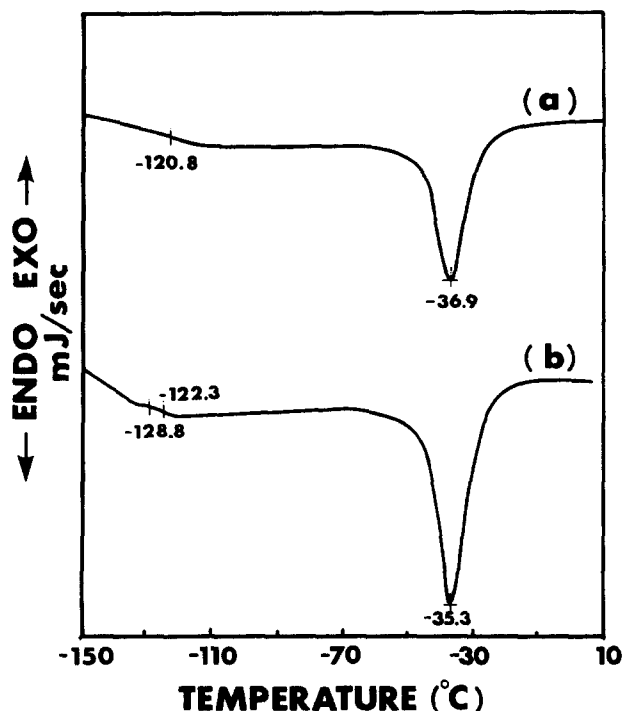


Figure 4 D.s.c. thermograms of PDMS networks: (a) bimodal network; (b) sequential full IPN

Transition behaviour

The thermal transition behaviour of linear prepolymers and crosslinked elastomers of PDMS was investigated by differential scanning calorimetry. The observed thermograms are illustrated in Figures 3 and 4. Glass transition and melting temperatures are given in Table 4.

As can be seen from Figures 3a and 3c, linear PDMS chains remain non-crystalline and elastomeric up to very low temperatures, the melting points of these samples, -32.8 and -35.1°C for PDMS-15 and PDMS-75, respectively. Linear PDMS prepolymers exhibit crystallization peaks around -80°C (-83.9 and -81.4°C for PDMS-15 and PDMS-75 respectively).

However, as expected, PDMS-15 has a sharper peak than PDMS-75. Obviously, crosslinked PDMS networks do not exhibit these crystallization peaks around -80°C . Fusion peaks of the melting points still appear around -40.9 and -37.3°C for PDMS-15 and PDMS-75 respectively.

As is known, the PDMS glass transition temperature is the lowest (-127°C) reported for any polymer⁴. The T_g value observed in this work for linear chains is identical with the value given in the literature.

Crosslinked PDMS networks have relatively higher T_g values. As is shown in Figures 3b and 3d, PDMS-15 network shows a T_g value higher than that of the PDMS-75 network, consistent with their relatively higher crosslink density.

The transition behaviour of bimodal network and sequential full interpenetrating network of PDMS has

Table 4 Glass transition and melting temperatures from d.s.c. data of linear and crosslinked PDMS elastomers

Sample designation	M_n, M_c (10^{-3} g mol $^{-1}$)	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)
PDMS-15	15	-127	-32.8
PDMS-75	75	-127	-35.1
Crosslinked PDMS-15	15	-96.7	-40.9
Crosslinked PDMS-75	75	-122.3	-37.3
Bimodal network	25	-120.8	-36.9
Sequential IPN	—	-128.8 -122.3	-35.3

also been examined. As shown in Figure 4, the bimodal network has one T_g value, which is barely observed at -121.3°C . On the other hand, the sequential full IPN sample exhibits two glass transition temperatures at -128.1 and -122.3°C . These values correspond to two distinct PDMS phases of IPN structures.

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