Investigation of the Conformation of Elastic Chains in Poly(dimethylsiloxane) Networks by Small-Angle Neutron Scattering

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ABSTRACT: Well-defined poly(dimethylsiloxane) networks containing a known fraction of labeled elastic chains were obtained by cross-linking mixtures of deuterated and undeuterated functional precursor polymers. Small-angle neutron scattering experiments on polymer melts, on semidilute solutions, and on dry and swollen networks show that the single intrachain form factor can be extracted from the scattered intensities even when the volume fraction of labeled polymer is high. The chain dimensions are not changed by the cross-linking process. The radius of gyration of an elastic chain in the unswollen network and that of the corresponding "free" chain in the melt are identical. The Gaussian character of the network chains has been confirmed with a high precision.

Introduction

Small-angle neutron scattering (SANS) is one of the most powerful tools to investigate the conformation of macromolecular chains in the condensed state. The technique of perdeuteration of polymer chains allows a visualization of a deuterated chain in an undeuterated polymer matrix. This method has been used with success to characterize the conformation of polymer chains in the bulk as well as that of elastic chains in a polymer network.

Until recently, the experimental investigations in the field of cross-linked systems carried out in our laboratory dealt mainly with model networks of polystyrene. Unfortunately, in the unswollen state, this polymer is quite inadequate for studies of chain conformation under stress, since such investigations have to be carried out in the elastic domain, i.e., above the glass transition temperature T_g, which is rather high for polystyrene.

The present article is devoted to a study by SANS on poly(dimethylsiloxane) (PDMS) networks containing known amounts of perdeuterated chains. This polymer is interesting in several respects. The PDMS chain is very flexible and its glass transition temperature is extremely low ($T_g \sim -120$ °C). The linear polymers are viscous liquids over a broad molecular weight range (up to $M \sim 10^5$). After cross-linking, the PDMS networks obtained are elastic over a large temperature range.

Experimental Section

A. Synthesis of Perdeuterated Monomers. Hexamethylcyclotrisiloxane (D_3) and Octamethylcyclotetrasiloxane (D_4). The synthesis of D_3 and D_4 has been achieved according to the following general reaction scheme:

$$\underset{\text{I}}{3CD_3OD} + {}^3/_2I_2 + P \rightarrow \underset{\text{II}}{3CD_3I} + D_3PO_3$$

$$CD_3I + Mg \xrightarrow{Et_2O} CD_3MgI$$

$$2CD_3MgI + Ph_2SiCl_2 \xrightarrow{Et_2O} \underset{\text{III}}{(CD_3)_2SiPh_2} + 2MgICl$$

$$\text{III} + HCl \xrightarrow[AlCl_3]{C_6H_6} \underset{\text{IV}}{(CD_3)_2SiCl_2} + 2C_6H_6$$

$$\text{IV} + nH_2O \xrightarrow{Et_2O} \underset{\substack{\text{V}\\ \text{linear + cyclic}\\ \text{siloxanes}}}{(\text{-}Si(CD_3)_2O\text{-})_n}$$

$$\text{V} + KOH \xrightarrow{\Delta} D_3 + D_4$$

The reaction conditions for the last step were chosen in order to increase the amount of D_4 formed.

Reagents. The starting material (I) was perdeuterated methanol of high isotopic purity (Spectrometrie, Spin et Techniques). The degree of deuteration is defined by the following ratio:

$$\%\ D = \frac{[\text{deuterium}]}{[\text{deuterium}] + [\text{hydrogen}]} = 99.7\%$$

Diphenyldichlorosilane (Ph_2SiCl_2) (Rhône-Poulenc Industrie) was distilled before use (purity 99%). The solvents used—diethyl ether and benzene—were dried on molecular sieves (4 Å) and distilled.

Perdeuterated Methyl Iodide (II). Compound II was prepared according to a classical method reported in the literature.[1] Perdeuterated alcohol I (6.2 mol, 250 mL) was reacted with iodine (6.2 mol, 786.6 g) in the presence of phosphorus (2.26 mol, ~70 g). The crude reaction product was washed successively with $NaHSO_3$, hydrochloric acid, and $NaHCO_3$ and then dried and distilled: bp 42 °C; yield 81%; degree of deuteration $99._7\%$).

Bis(trideuteriomethyl)diphenylsilane (III). Compound III was prepared by a Grignard reaction:[2] A solution of 4.03 mol (583.5 g) of CD_3I in 600 mL of ether was introduced dropwise into a glass reactor containing an excess of magnesium chips and 250 mL of diethyl ether (under gentle reflux). The Grignard solution obtained was first titrated and then added slowly to a stoichiometric quantity of Ph_2SiCl_2 dissolved in 250 mL of ether. After completion of the reaction, the medium was hydrolyzed. The ether solution was washed and dried. After removal of the ether, the silane III obtained was distilled under low pressure (1.9 mmHg): bp 108 °C (1.9 mmHg); yield 80%; purity determined by vapor pressure chromatography, 99%. ^1H NMR measurements revealed no undeuterated methyl groups.

Dimethyldichlorosilane (IV). Aluminum chloride (5 g) ground under an inert atmosphere and 300 mL of benzene were placed in a four-neck glass reactor. The benzene solution was saturated with gaseous hydrochloric acid. The reaction medium was then cooled to 15 °C and kept at this temperature during the slow, dropwise addition of 300 mL of compound III (which requires about 5 h). The HCl saturation has to be maintained during the reaction. After this addition a few milliliters of acetone was added to destroy the aluminum chloride, and part of the excess HCl was evacuated by means of a nitrogen flow. The dichlorosilane IV obtained was isolated by distillation: yield 90%; purity determined by vapor pressure chromatography, 99.7%.

Synthesis of Cyclic Tri- and Tetrasiloxanes (V). Hydrolysis of Compound IV. A solution of 270 mL of IV in 250 mL of ether and 600 mL of water were poured simultaneously at the same rate into a vigorously stirred mixture of 100 mL of HCl (7 N) and 100 mL of ether. The temperature was maintained around 30 °C. The hydrolysis reaction yielded an oily mixture of various perdeuterated siloxanes, mainly cyclic ones. The composition of this mixture was determined by gas chromatography (VPC): hexamethylcyclotrisiloxane (D_3-d_{18}), 2%; octamethylcyclotetrasiloxane (D_4-d_{24}), 83%; decamethylcyclo-

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Table I
Characteristics of PDMS Precursors Determined by IR Spectroscopy, Light Scattering, and GPC

sample	M_n(IR)	M_w(LS)	M_w/M_n	M_z/M_w (GPC)
D1	3 100	4 700[a]		1.44
D2	6 100	10 000	1.64	1.49
D3	10 500	16 700	1.59	1.50
D4	23 000	34 000	1.48	1.50
H1	3 050	5 400	1.77	
H2	6 400	10 900	1.70	1.44
H3	9 700	15 600	1.58	1.41
H4	25 000	35 000	1.40	1.51

[a] From GPC diagram.

Table II
Characteristics of the PDMS Networks[a]

f	$M_{n,D}$	$M_{n,H}$	φ_D	v_c	w_s	w_u
4	10 500	9 900	0.0202	0.71	0.038	0.006
	10 500	9 900	0.0782	0.71	0.041	0.007
	10 500	9 900	0.1962	0.71	0.038	0.004
	10 500	9 900	0.4969	0.71	0.040	0.005
4	3 100	3.050	0.1889	0.71	0.040	0.004
4	6 100	6 400	0.1962	0.71	0.043	0.010
	6 100	6 400	0.1890	1.00	0.040	0.003
4	10 500	9 700	0.1880	0.60	0.047	0.009
	10 500	9 700	0.1882	1.00	0.038	0.003
4	23 000	25 000	0.1875	0.71	0.049	0.017
	23 000	25 000	0.1885	1.00	0.046	0.009
6	10 500	9 700	0.1874	1.00	0.047	0.002
	10 500	9 700	0.2676	0.71	0.048	
6	23 000	25 000	0.0760	1.00	0.055	

[a] φ_D = fraction of perdeuterated chains, v_c = polymer volume fraction at gel formation, w_s = total amount of extractable compounds, w_u = fraction of unreacted precursor polymer, and f = functionality of the junctions.

pentasiloxane (D_5-d_{30}), 10%; other siloxanes, 4% (D_3, D_4, and D_5 are the commonly used symbols for cyclic siloxanes and d_n represents the number of deuterium atoms in the compound).

Thermal Treatment. The proportion of trimeric and tetrameric cycles in the previous siloxane mixtures can be increased by the following thermal treatment: 150 mL of the silicone oil was introduced dropwise into a reaction vessel containing 10 g of potassium hydroxide heated to about 140–150 °C under low pressure (20 mmHg). The resulting mixture exhibited the following composition: D_3-d_{18}, 5%; D_4-d_{24}, 92%; D_5-d_{30}, 3%. The yield determined on the basis of initial compound IV is 87%.

A final rectification yields octamethylcyclotetrasiloxane of high purity: 99.98%; bp 92 °C (53 mmHg). Mass spectrometry indicates an almost total deuteration: % D = 99.7%. The overall yield for the five-step synthesis was calculated on the basis of the initial quantity of deuterated alcohol I: 51%.

B. Synthesis and Characterization of α,ω-Functional Poly(dimethylsiloxanes). Synthesis. Octamethylcyclotetrasiloxane (D_4 or D_4-d_{24}) was polymerized cationically in the presence of 1,3-dihydrogeno-1,1,3,3-tetramethyldisiloxane. The latter compound, acting as a transfer agent, allows the average degree of polymerization to be set at a given value and incorporation of >SiH functions at both ends of the PDMS chains formed. The reaction conditions were derived from those currently used in industrial synthesis. The polymer obtained contains approximately 10% small cyclic molecules such as D_4, D_5, and D_6 and their linear homologues. Heating to 100 °C under reduced pressure allows elimination of the major part of them. After this treatment the polymer still contains about 3% cycles, which do not participate in the cross-linking reaction used for network synthesis.

Perdeuterated and undeuterated PDMS samples were prepared covering a molecular weight range from 3000 to 25 000.

Characterization of the α,ω-Functional PDMS Samples. Infrared Spectroscopy. Infrared spectroscopy allows a rather accurate determination of the number of terminal >SiH functions present in the polymer: the Si–H linkages give rise to a strong absorption band at 2130 cm^{-1}, which is rather far from the other absorption bands present in the spectrum. In the concentration range considered here, this absorption band follows the Lambert–Beer law.

The number-average molecular weights M_n of the polymers were calculated from the values given by the IR titration.

The weight-average molecular weights of the PDMS samples were determined by light scattering measurements on toluene solutions.

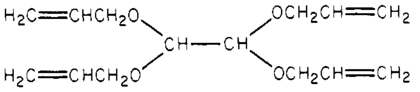
Gel Permeation Chromatography (GPC). GPC experiments were carried out in toluene using a Waters Chromatograph with refractometric detection and equipped with two μ-Styragel columns (Shodex A 80 M).

The molecular weight determination by GPC is approximate since it is based on polystyrene calibration. The peak that arises from small cyclic species in the GPC diagrams was not taken into account for the calculation of the molecular weight.

The main characteristics obtained for our PDMS samples are summarized on Table I.

C. Synthesis of the Networks. The PDMS networks were prepared by end-linking of the above-mentioned α,ω-functional precursor polymers. This synthesis is based on the addition reaction of a >SiH group onto a vinyl or allyl double bond (hydrosilylation reaction). A network containing a given proportion of deuterated chains is obtained by reacting a mixture of known amounts of deuterated and nondeuterated PDMS precursor chains with a tetrafunctional or hexafunctional cross-linker under stoichiometric conditions.[3] The catalyst used is chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, Prolabo). The tetrafunctional cross-linking agent VI, tetraallyloxyethane (Nobel-Hoechst), was treated first with sodium and then distilled over sodium wire.

Pure oxybis[3-(allyloxy)-2,2-bis[(allyloxy)methyl]propane] (VII), the hexafunctional cross-linker, was prepared in the laboratory.[4] Toluene was used as solvent.



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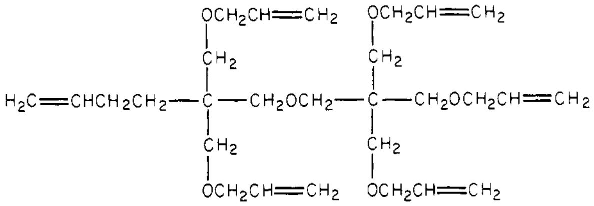

VII

The networks always contain a small amount of soluble polymer, which can be eliminated by toluene extraction. A GPC analysis of the extractable fraction indicates that it contains mainly small cycles, present in the precursor polymers. Besides these unreactive cyclic compounds, the actual amount of unreacted precursor is very small. More details concerning this point will be reported elsewhere.

In Table II, we have listed the characteristics of the networks used in the present investigation, the total amount w_s of extractable compounds and the fraction of unreacted precursor polymer w_u.

D. Small-Angle Neutron Scattering Experiments. Small-angle neutron scattering (SANS) experiments have been carried out on (i) samples of a given molecular weight $M_n \sim 10000$ and (ii) samples containing a given volume fraction of PDMS(D) ($\varphi_D \sim 0.2$). In category i, the following samples were used: (a) blends of linear PDMS(D) and PDMS(H) containing various volume fractions φ_D of labeled chains; (b) the corresponding networks prepared in toluene at an overall concentration by volume of $v_c = 0.71$ and dried subsequently. Category ii consisted of the following samples: (a) blends of linear PDMS(D) and PDMS(H) of identical molecular weight ($M_n \sim$ 3000, 6000, 10 000, and 25 000); (b) the corresponding tetrafunctional networks cross-linked at several volume fractions v_c (v_c ranging from 0.6 to 1) and dried subsequently; (c) hexafunctional networks corresponding to two of the above blends ($M_n \sim$ 10 000 and 25 000). Disk-shaped samples of about 1 mm thickness and 10 mm diameter were used for the scattering measurements. The neutron scattering experiments were performed on the D11A and D17 instruments of the Institute Von Laue-Langevin (Grenoble, France), the momentum transfer q ($q = (4\pi/\lambda) \sin(\theta/2)$) ranging from 10^{-2} to 10^{-1} Å^{-1}.

The coherent scattering contribution was obtained by appropriate subtraction of the incoherent scattering (sample transmission was taken into account) and normalization by means of a flat incoherent scattering intensity over the whole range of q investigated (a 1-mm-thick water standard).

SANS Experimental Results

Measurement of the Single-Chain Form Factor: Use of High Volume Fractions of Labeled Chains. It was shown both theoretically[5,6] and experimentally[7,8] that the scattering of a bulk mixture of undeuterated and deuterated chains is directly proportional to the single intrachain scattering function $P(q)$. The scattering intensity can be written as

$$I(q) \sim (b_{\mathrm{D}} - b_{\mathrm{H}})^2 N\varphi_{\mathrm{D}}(1 - \varphi_{\mathrm{D}})P(q) \qquad (1)$$

where b_{D} and b_{H} are the coherent scattering lengths per unit of the deuterated and the undeuterated species, respectively, N is the total number of chains in the medium and φ_{D} the volume fraction of deuterated material.

The theoretical treatment has been extended to the case of three-component mixtures[5,6] and particularly to the case of two polymers differing only in their coherent scattering lengths (b_{D} and b_{H}) and immersed in a solvent S (b_{S}). The calculations lead to the following expression of the scattered intensity:

$$I(q) \sim N\varphi_{\mathrm{D}}(1 - \varphi_{\mathrm{D}})(b_{\mathrm{D}} - b_{\mathrm{H}})^2 P(q) + N(b_0 - b_{\mathrm{S}})^2[P(q) + NQ(q)] \qquad (2)$$

in which the average scattering length of the polymer mixture $b_0 = \varphi_{\mathrm{D}} b_{\mathrm{D}} + (1 - \varphi_{\mathrm{D}})b_{\mathrm{H}}$ and the intermolecular scattering function $Q(q)$ have been introduced.

As suggested by Akcasu et al.[5] one can adjust the coherent scattering length of the solvent by using appropriate compositions of isotopic species in such a way that $b_{\mathrm{S}} = b_0$. In this case, the second term of eq 2 cancels out and thus the intramolecular scattering function can be obtained whatever may be the polymer concentration.

These equations have been established and used in the case of mixtures of identical chains, regardless of their statistical laws. It is quite evident that the demonstration of eq 1 and 2 is also valid if the chains are cross-linked, either randomly or by an end-linking reaction, as long as there are no differences between labeled and unlabeled chains.

Until recently, SANS experiments were carried out on networks containing low volume fractions of deuterated species[9,10] in order to decrease the probability of two labeled chains being linked to the same cross-link.

The aim of the present SANS experiments was to check the validity of the above expressions both on linear PDMS in the bulk or in semidilute solutions and in the case of PDMS networks, swollen or not.

Single-Chain Form Factor from Blends and Networks. Figure 1 shows the variation of the scattered intensities for PDMS(D)–PDMS(H) blends and networks as a function of q for various volume fractions φ_{D} of labeled species. The intensities have been divided by the quantity $\varphi_{\mathrm{D}}(1 - \varphi_{\mathrm{D}})$ according to eq 1. With this representation one should obtain the form factor $P(q)$ for any value of φ_{D}.

The scattering intensities at $q = 0$ are obtained by zero extrapolation on Zimm-type representations (I^{-1} vs. q^2).

Within the limits of experimental accuracy, the curves corresponding to the four values φ_{D} of the volume fractions studied are intermingled, as well in the case of blends as in the case of networks.

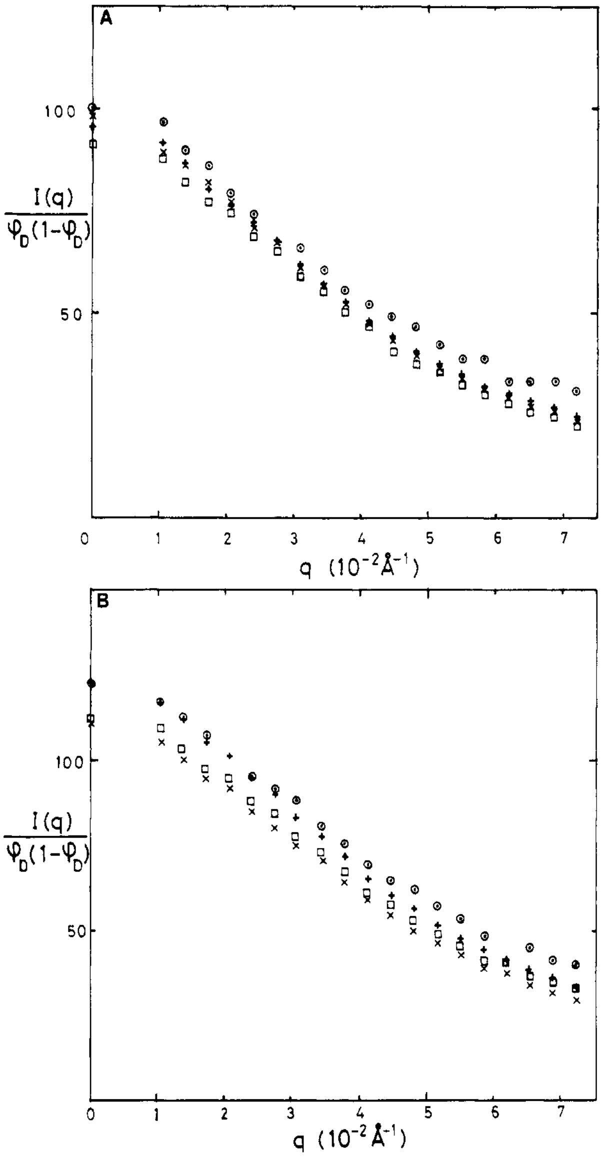

Figure 1. (A) Scattered intensities $I(q)/[\varphi_{\mathrm{D}}(1 - \varphi_{\mathrm{D}})]$ as a function of the momentum transfer q for four values of φ_{D} for the polymer melts ($M_{\mathrm{n}} \sim 10\,000$): (+) $\varphi_{\mathrm{D}} = 0.4784$; (×) $\varphi_{\mathrm{D}} = 0.1880$; (□) $\varphi_{\mathrm{D}} = 0.0742$; (⊙) $\varphi_{\mathrm{D}} = 0.0182$. (B) Scattered intensities $I(q)/[\varphi_{\mathrm{D}}(1 - \varphi_{\mathrm{D}})]$ as a function of the momentum transfer q for four values of φ_{D} for the networks corresponding to the melts in Figure 1A: (+) $\varphi_{\mathrm{D}} = 0.4969$; (×) $\varphi_{\mathrm{D}} = 0.1962$; (□) $\varphi_{\mathrm{D}} = 0.0782$; (⊙) $\varphi_{\mathrm{D}} = 0.0202$.

Single-Chain Form Factor from PDMS Solutions and Swollen Networks. Scattering experiments were carried out on networks swollen to equilibrium in cyclohexane and on solutions of linear PDMS at an equivalent total polymer concentration. In both cases the isotropic composition of the solvent was adjusted in order to fulfill the condition $b_{\mathrm{S}} = b_0$.

Figure 2 shows, as previously, the standard representation of $I(q)/\varphi_{\mathrm{D}}(1 - \varphi_{\mathrm{D}})$ for the swollen networks and the corresponding solutions. Again, as in the case of blends and dry networks, the curves obtained are intermingled. It must be noted that the superposition of the scattering curves is better for the blends and for the solutions than for the corresponding dry or swollen networks.

In the first case (Figures 1A and 2A) the small discrepancies are mainly due to random errors on the scattering measurements.

In the case of networks the measurements of the sample thickness and the determination of the swelling ratio in-

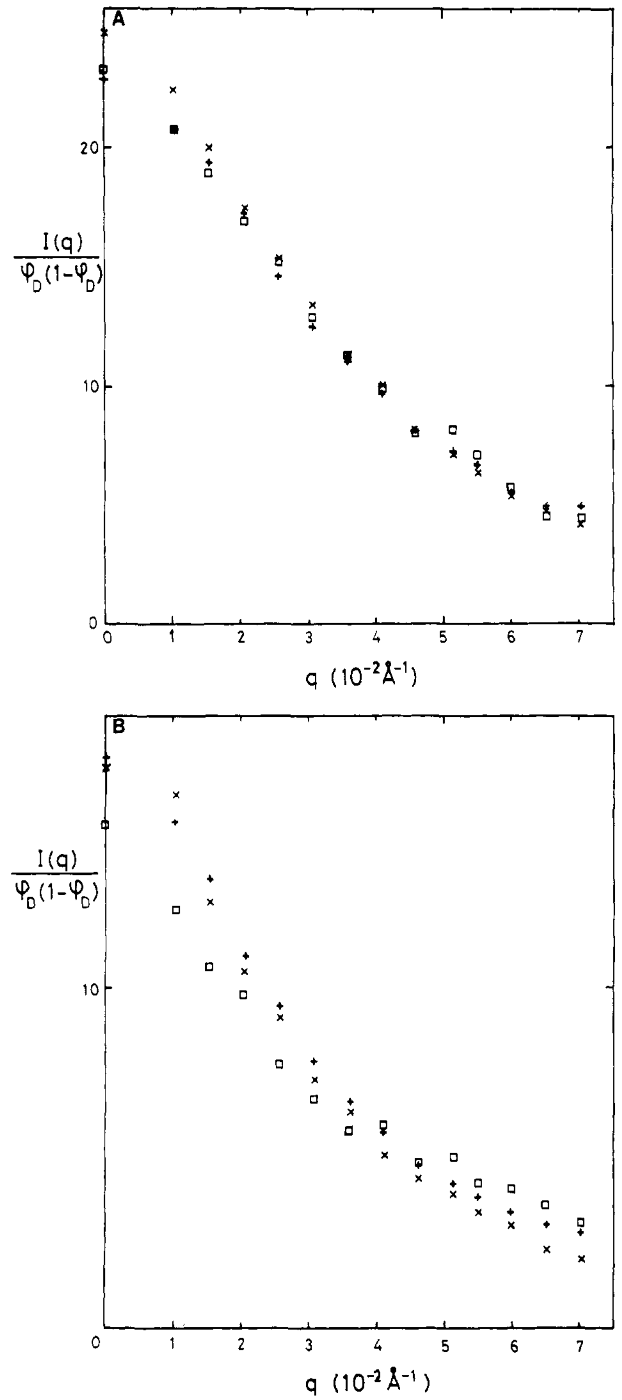

Figure 2. (A) *$I(q)/[\varphi_D(1-\varphi_D)]$ as a function of q corresponding to semidilute solutions ($M_n \sim 10000$, $v_c = 0.71$) for three values of φ_D: (+) $\varphi_D = 0.4784$; (×) $\varphi_D = 0.1880$; (□) $\varphi_D = 0.0742$.* (B) $I(q)/[\varphi_D(1-\varphi_D)]$ as a function of q corresponding to the swollen networks ($M_n = 10000$) for three values of φ_D: (+) $\varphi_D = 0.4969$; (×) $\varphi_D = 0.1962$; (□) $\varphi_D = 0.0782$.

troduce additional errors. It follows that the evaluation of the background correction is somewhat less accurate. That is why larger discrepancies appear on Figures 1B and 2B.

Radii of Gyration. The Zimm representation (see Figure 3) allows the determination of the mean square radius of gyration $\langle R_g^2\rangle$:

$$[P(q)]^{-1} \cong 1 + q^2(\langle R_g^2\rangle/3) \qquad \text{for } q^2\langle R_g^2\rangle \ll 1 \quad (3)$$

In Table III we have listed the experimental values of $\langle R_g^2\rangle^{1/2} = R_g$ obtained for the blends and for the dry networks. It is clearly demonstrated that no concentration dependence affects the mean dimensions measured.

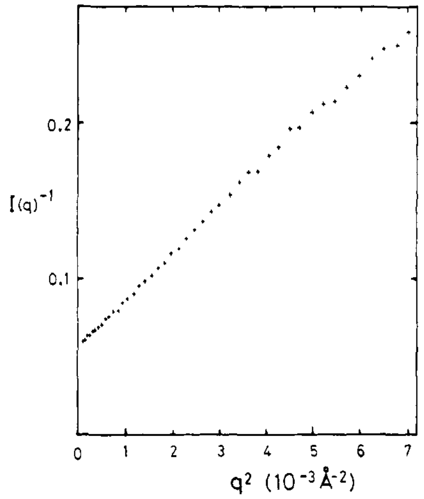

Figure 3. Inverse scattered intensity $I^{-1}(q)$ as a function of the square momentum transfer q^2 for a network containing 20% PDMS(D) ($M_n \sim 10000$).

Table III
Experimental Values of $R_g = \langle R_g^2\rangle^{1/2}$ for Precursor Chains in Polymer Blends and for Elastic Chains in Dry Networks

	R_g, Å	
φ_D	blends	networks
0.02	40	36
0.08	41	38
0.2	41	39
0.5	41	39

For the lowest PDMS(D) contents (2–5%) the experimental accuracy is of the order of 10% whereas in the samples containing approximately 50% deuterated PDMS, the experimental error is lower than 5%.

It follows from the above experimental results that the validity of eq 1 and 2 extends not only to mixtures of labeled and unlabeled chains in the bulk or in solution but also to elastic chains linked by their ends in a network (both in the dry and in the swollen state).

The important advantage of the use of samples containing high volume fractions of labeled chains is that the ratio of the coherent signal to the incoherent background is highly enhanced.

As a consequence, the accuracy of the measurements can be improved very much while the neutron beam exposure time can be reduced considerably: the maximum in coherent scattering intensity occurs for a 50:50 mixture of deuterated and undeuterated species (this can be seen from the parabolic dependence of $I(0)$ corresponding to the dry networks on φ_D shown in Figure 4).

All the following experiments were carried out on samples containing about 20% of PDMS(D).

Remark: Influence of the Polydispersity on the SANS Measurements. Equations 1 and 2 are valid for mixtures of deuterated and undeuterated polymers of identical molecular weights. In the system that we have investigated, the molecular weight distributions of the deuterated and the undeuterated species are not strictly the same (see Table I). It follows that the radius of gyration measured corresponds to an apparent value. According to Boué et al.,[8] this apparent value is related to the real one by the following expression:

$$\langle R_g^2\rangle_{app} = \frac{N_{zD}a^2}{6}\left(1 + \frac{\varphi_D \Delta Z}{1 + (1-\varphi_D)\Delta w}\right) \qquad (4)$$

where

$$\Delta w = N_{wH}/N_{wD} - 1$$

and

$$\Delta Z = N_{zH}/N_{zD} - 1$$

If we set

$$\frac{\varphi_D \Delta Z}{1 + (1 - \varphi_D)\Delta w} = F$$

then

$$\langle R_g^2 \rangle_{app} = \langle R_z^2 \rangle (1 + F) \tag{5}$$

Thus the relative error on $\langle R_z^2 \rangle^{1/2}$ is $F/2$. For the sample used in the present investigation this error was negligible ($0.001 < F/2 < 0.025$).

Influence of Cross-Linking on the Conformation of the Elastic Chains in the Dry Network. Radius of Gyration: Guinier Range of q. The conformation of a linear polymer chain in the bulk has been extensively investigated and is now well-known. Several SANS studies have shown clearly that the statistics of the chains in the bulk state is Gaussian.[11-14]

But the influence of cross-linking on the dimensions of a chain still remains subject to many controversial discussions. Therefore it was of interest to establish whether or not cross-linking induces a modification of the average dimensions of a chain when it becomes a network chain upon end-linking. In the present SANS investigation, we have measured the radius of gyration (R_g) of PDMS chains in the melt. Four samples of different molecular weights have been considered. The values of R_g obtained were compared to those determined for the same chains after cross-linking.

The characteristics of the networks investigated are gathered in Table II. The experimental radii of gyration R_g of network chains and of free chains in the melt are listed in Table IV.

In Figure 5 we have plotted the scattered intensities vs. q for the cross-linked samples prepared at three concentrations v_c (using precursor polymers of molecular weight $M_n = 10\,000$) and for the corresponding free polymer: all experimental points fit the same curve within the accuracy of the measurements.

Thus it appears clearly that cross-linking does not influence significantly the dimensions R_g of the chains. This result is independent of the concentration v_c at which the network is formed.

If we assume that the elastic chains are Gaussian, R_g^2 should obey the relation

$$R_g^2 = kM \tag{6}$$

The experimental values of R_g correspond to z averages, whereas the molecular weights M_w determined by light scattering are weight averages. In order to get a consistent representation, we have corrected the radius of gyration measured R_g by the factor $(M_z/M_w)^{1/2}$, calculated from the GPC diagrams.

The values R_w thus obtained and the corresponding weight-average molecular weights are gathered in Table V.

In Figure 6 we have plotted on a double-logarithmic scale R_w as a function of M_w for the melts and for the networks. Mean square extrapolation leads to the following relations between R_w and M_w:

$$R_w = 0.23 M_w^{0.51} \quad \text{(melts)} \tag{7}$$

$$R_w = 0.25 M_w^{0.50} \quad \text{(networks)} \tag{8}$$

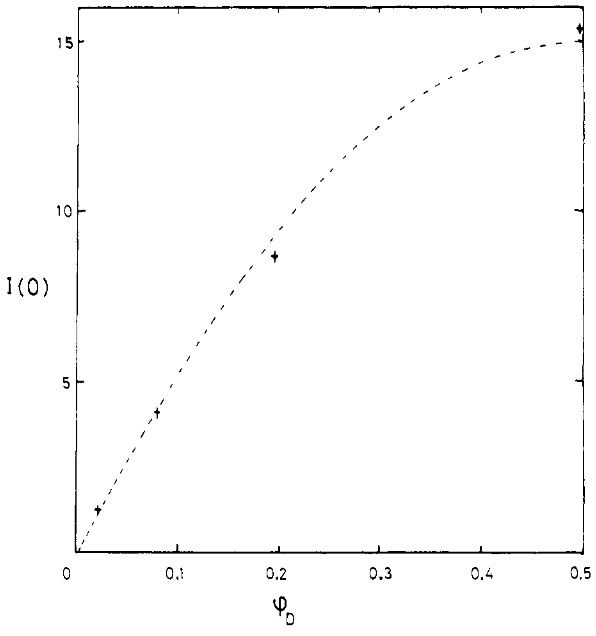

Figure 4. Scattered intensities extrapolated to $q = 0$. $I(0)$ as a function of φ_D for the networks in Figure 1B. The dashed line represents the parabolic curve calculated by mean-square analysis.

Table IV
Comparison of the Radii of Gyration R_g of the Network Chains with Those of the Corresponding Free Chains in the Melt[a]

		R_g(network), Å				
		hexa-functional		tetrafunctional		
M_n	R_g-(melt), Å	$v_c = 1.00$	$v_c = 0.71$	$v_c = 1.00$	$v_c = 0.71$	$v_c = 0.60$
3 000	22				22	
6 000	31.5			32	31.5	
10 000	41	41	39	41	39	39
23 000	61	59		60	60	

[a] v_c = polymer volume fraction at network formation.

Table V
Radii of Gyration Corrected by the Factor $(M_z/M_w)^{1/2}$ Calculated from the GPC Diagrams

		R_w, Å	
M_n	M_w	melt	network
3 100	4 700	18	18
6 100	10 000	26	26
10 500	16 700	33	33
23 000	34 000	50	49

Intermediate Range of q. In order to corroborate the Gaussian character of the PDMS chains in the bulk and in the dry network, we have studied a network prepared in the bulk and the corresponding linear polymer ($M_n = 10\,000$) in the intermediate range $1/R_g < q < 1/b$ (b is the length of the statistical element). In this domain, $I(q)$ can be written as[15]

$$I(q) \sim K/q^{1/\nu} \tag{9}$$

For a Gaussian coil $\nu = 1/2$ and consequently

$$I(q) \sim K/q^2 \tag{10}$$

In Figure 7 we have plotted $I^{-1}(q)$ vs. q^2 ($4 \times 10^{-4} \le q^2 \le 2.2 \times 10^{-2}$ Å^{-2}) for the two above samples.

The corresponding curves are superimposable. The dashed line on the plot corresponds to the Debye function

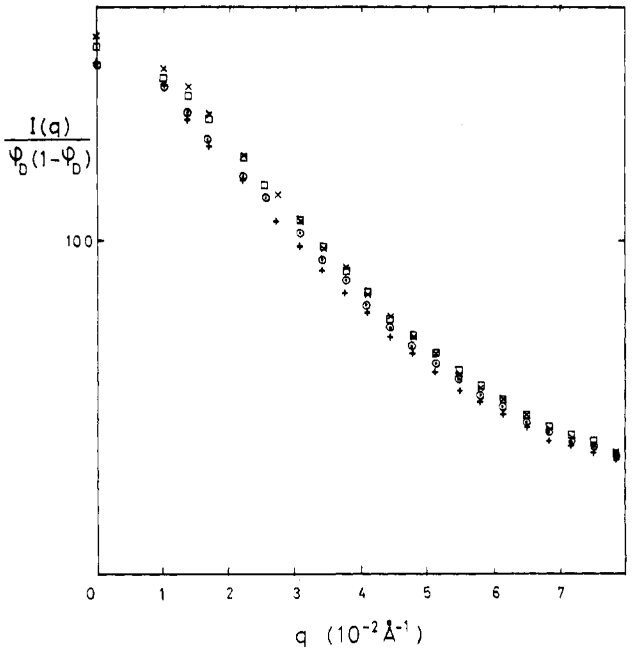

Figure 5. $I(q)/[\varphi_D(1 - \varphi_D)]$ as a function of q for the melt ($M_n \sim 10000$) (+) and the corresponding networks cross-linked at three concentrations: (×) v_c = 1.00; (□) v_c = 0.71; (⊙) v_c = 0.60.

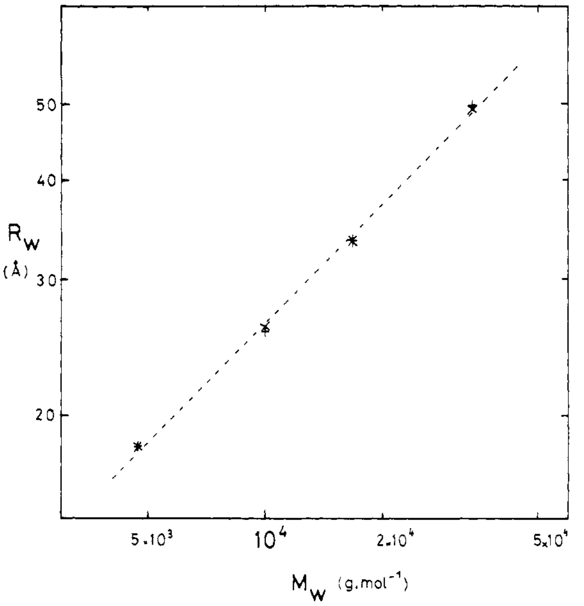

Figure 6. log-log plot of the radius of gyration R_w as a function of the weight-average molecular weight M_w for the melts (+) and the corresponding networks (×).

of a Gaussian coil with radius of gyration R_g = 41 Å and for which account was taken of polydispersity (assuming a Schulz distribution of the molecular weights[16,17]).

The plot of $q^2 I(q)$ vs. q shown in Figure 8 confirms the Gaussian character of the PDMS chains both in the melt and in the rubbery network.

Conclusion

Pure perdeuterated cyclic dimethylsiloxanes (D_3-d_{18} and D_4-d_{24} were obtained in good yields by a five-step synthesis. The ring-opening polymerization of the D_4-d_{24} compounds in the presence of 1,3-dihydrogenodisiloxane leads to perdeuterated poly(dimethylsiloxanes) with $\geqslant$SiH functions.

Well-defined networks containing known fractions of labeled PDMS chains were obtained by cross-linking mixtures of deuterated and undeuterated functional precursor polymers using tetra- and hexafunctional cross-linking agents.

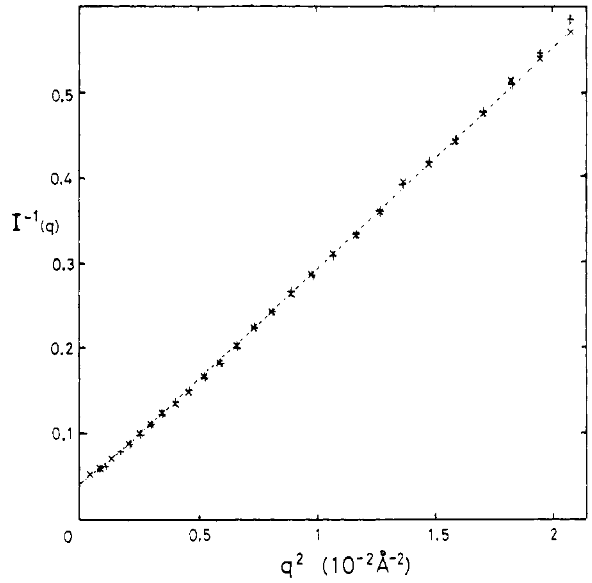

Figure 7. $I^{-1}(q)$ as a function of q^2 for the melt ($M_n \sim 10000$) (+) and the corresponding network (v_c = 1.0) (×) in the intermediate range. The dashed line represents a Debye function (see text).

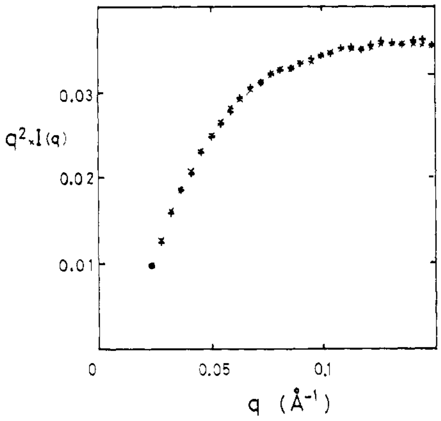

Figure 8. $q^2 I(q)$ as a function of q for the melt (+) and the corresponding network (×) of Figure 7.

Samples were prepared at polymer concentrations v_c covering the range 0.6–1 in order to establish whether entanglements in precursor chains get trapped upon cross-linking.

An investigation by SANS on polymer melts, on semidilute solutions, and on dry and swollen networks has shown that the single intrachain form factor can be extracted from the scattered intensities even when the volume fraction of labeled polymer is high. As a consequence, the exposure time of the samples can be reduced considerably, still improving noticeably the accuracy of the measurements.

For three-component systems (solutions and swollen networks) the isotopic composition of the solvent has to be chosen in order to cancel the intermolecular term.

An important result of the present investigation is that the chain dimensions are not changed upon cross-linking by an end-linking process: the radius of gyration of an elastic chain in the dry network and that of the corresponding "free" chain in the melt are the same within the limits of experimental accuracy. This is true as well for networks prepared in the bulk as for systems cross-linked in solution.

The Gaussian character of the conformation of the elastic chains has been verified with a high precision.

Further results related to experiments carried out on systems submitted to uniaxial deformation and on swollen networks will be reported in forthcoming publications.

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Crystalline Order in Copolymers of Ethylene and Propylene

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ABSTRACT: Copolymers of ethylene and propylene in which none of the propylene units are reversed have low levels of crystallinity over the entire range of composition. Molecular mechanics calculations indicated that the polyethylene-type planar-zigzag conformation and the polypropylene-type helical conformation would have similar energies in copolymers containing 33–55 mol % ethylene. Measurements by X-ray diffraction and differential scanning calorimetry showed that samples in this range contained both kinds of crystals. When a copolymer of propylene with 36 mol % ethylene was incorporated in a blend of isotactic polypropylene and low-density polyethylene, the polyethylene phase was more finely dispersed, and the interfacial adhesion and notched Izod impact strength were improved. These effects were attributed to the ability of the copolymer to cocrystallize with both homopolymers.

Introduction

Copolymers of ethylene and propylene involve a surprising number of structural variables. First, one is concerned with the fractions of the two monomer units. Then there is the question of their distribution in the polymer chains. A great deal of information about this can be obtained by carbon-13 NMR.[1-3] The propylene units may all add head-to-tail, or some of them may be reversed. Reversals are revealed by the presence of sequences of even numbers of methylene units between branch points. In copolymers made with vanadium-based catalysts, a significant fraction of the propylene units is reversed.[1,4] When a titanium-based catalyst is used, this does not occur at a detectable level.[2,4] Finally, one should consider the tacticity of any sequences of propylene units.

It is well-known that a certain number of methyl side groups can be accomodated in a polyethylene-type crystal through expansion of the unit cell along its *a* axis.[5-9] In this case, the conformation of the chain remains all-trans planar zigzag. On the other hand, in isotactic polypropylene, the conformation is a 3-fold tgtgtg helix, which serves to minimize the interactions between adjacent methyl groups. A copolymer having a low [E]/[P] ratio is equivalent to a polypropylene from which a few methyl groups have been removed. It would not be surprising to find that a polypropylene crystal could tolerate a certain number of defects of this type. However, at some point, the polyethylene-type conformation should become preferred. It is the purpose of this paper to examine the competition between the helical and planar conformations.

Polymer Modeling via Molecular Mechanics

We have addressed the problem outlined above by studying oligomers incorporating the principal features of interest in polypropylene and ethylene–propylene copolymers. (At this point, we are concerned with the energies of various conformations for isolated molecules in the gas phase. The effect of crystal packing will then be addressed experimentally through studies of the properties of copolymers.) Models were generated in various conformations which were then refined with the molecular mechanics program MM1.[10] This program incorporates the 1973 Allinger force field[11] and refines the starting coordinates, seeking the nearest minimum-energy state.

This methodology has been successfully applied to a wide variety of compounds, most notably hydrocarbons of

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