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Model polydiethylsiloxane networks: 1. Synthesis and phase behaviour

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The preparation and hydrosilylation crosslinking of well-defined vinyl and allyl polydiethylsiloxane (PDES) telechelics are described. End functionalization has been achieved by using divinyltetramethyldisiloxane as a chain stopper during the cationic polymerization of hexaethylcyclotrisiloxane or by anionic polymerization of hexaethylcyclotrisiloxane with allyllithium followed by end capping with allyldimethylchlorosilane. Hydrosilylation crosslinking yielded model PDES networks which have been characterized by equilibrium swelling, determination of the sol fraction, differential scanning calorimetry and wide angle X-ray diffraction.

(Keywords: PDES networks; hydrosilylation; crosslinking)

INTRODUCTION

Recent studies on model polydimethylsiloxane (PDMS) networks have shown the influence of network regularity on the stress–strain behaviour and ultimate strength[1–3]. It is expected that the network topology will have important consequences for networks capable of self-organization. So far, research on liquid crystalline networks has been focused mainly on materials prepared from side-chain liquid crystalline polymers[4–6]. A number of previous investigations have been directed towards networks based on polydiethylsiloxane (PDES) which exhibits a columnar mesophase[7–9]. This peculiar mesomorphic behaviour is based on the conformational disordering of the polymer main chain and side groups[10]. Calorimetric studies on the stress–strain behaviour of PDES elastomers revealed a remarkably strong stress dependence of the isotropization temperature. Compared with the stress-induced crystallization of crystallizable rubbers, for which usually a 10–30°C increase in the crystallite melting temperature is observed[11], the increase in the PDES isotropization temperature is much larger and may exceed 100°C. This has been explained in terms of the rather small enthalpy changes involved in formation of the mesophase from the isotropic melt[8,9].

Linear uncrosslinked PDES has been extensively investigated with regard to its melting behaviour[12–14]. Depending on the rate of cooling, PDES displays a kinetically formed monoclinic α-crystal modification or a thermodynamically stable tetragonal β-crystal modification. Both modifications show two polymorphs (α_1, α_2 and β_1, β_2) which are separated by a first-order crystal–crystal transition. The α_2-crystal and β_2-crystal structures transform in the same columnar mesophase (μ-phase), which upon further heating finally melts into an isotropic liquid. The isotropization temperature appears to be strongly molecular weight dependent[12,13], attaining a maximum value of about 326 K for samples with $M_w > 200\,000$ g mol^{-1}.

Introduction of crosslinks by peroxide vulcanization of PDES leads to exclusive formation of the α-modification upon crystallization of the network[12,13]. No systematic investigation of the phase behaviour of PDES networks in relation to the network topology has been undertaken so far. In this paper we consider whether the numbers of crosslinks and irregularities in the network structure affect the phase behaviour in a similar manner to that established for linear uncrosslinked PDES for the influence of molecular weight[12,13]. This knowledge might help us to understand the influence of crosslink density on the mechanical behaviour of PDES networks, which will be the subject of a forthcoming paper.

EXPERIMENTAL

Materials

Hexaethylcyclotrisiloxane (D_3Et_2) was prepared as described eleswhere[15], distilled from CaH_2 and subsequently kept under argon. Trifluoromethanesulfonic

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acid (triflic acid, CF_3SO_3H) (Alfa) was freshly distilled under vacuum before its use as an initiator. Divinyltetramethyldisiloxane (M_vM_v) (Aldrich) was distilled from CaH_2. The SiH crosslinking agent, a branched hydromethylsiloxane oligomer with the average formula $[SiO_{4/2}]_4[SiO_{1/2}(CH_3)_2H]_8$ [16], the platinum cyclovinylmethylsiloxane complex PC085 (Hüls), allyldimethylchlorosilane (Aldrich, 98%), allyltriphenyltin (Aldrich, 99%) and phenyllithium (Aldrich, 1.8 M in pentane/diethyl ether) were used as received. Kryptofix [211] (Aldrich) was distilled under high vacuum conditions in a quartz distillation apparatus and subsequently stored under argon at −20°C. Toluene, diethyl ether and n-hexane were distilled from sodium/benzophenone and kept under argon.

Preparation of allyllithium

The preparative procedure described by Seyferth and Weiner[17] was followed. A 250 ml three-necked flask equipped with a stirring bar and argon inlet was charged with 25 g (0.0639 mol) of allyltriphenyltin and 140 ml of absolute diethyl ether. To the resulting slightly turbid solution was slowly added 35.5 ml (0.0639 mol) of 1.8 M phenyllithium in pentane/diethyl ether at room temperature. A thick grey suspension was formed instantaneously. After 1 h of stirring, the suspension was allowed to settle and the red-brown supernatant was carefully isolated by means of a syringe. The allyllithium concentration was determined to be 0.3 M (82% yield) by titration with acetanilide/triphenylmethane in dimethyl sulfoxide[18]. The solution was stored under argon at −20°C.

Preparation of PDES-22 using triflic acid and M_vM_v

A 100 ml two-necked flask equipped with an argon inlet, septum and stirring bar, was charged with 53 g (520 mmol of diethylsiloxane units) of hexaethylcyclotrisiloxane. After the monomer had been degassed three times, 488 μl (2.1 mmol) of M_vM_v was added through the septum. The mixture was homogenized by stirring for 5 min, followed by addition of 19 μl (0.21 mmol) of triflic acid. The polymerization was allowed to proceed for five days and then stopped by pouring the slightly red-brown viscous fluid into 1 l of ethanol to which several millilitres of triethylamine had been added. Cyclic by-products and traces of initiator were removed by repeated extraction in refluxing ethanol. The polymer was dried under vacuum at 110°C. The yield was 42.2 g (80%) ($M_n = 22\,000\,g\,mol^{-1}$, $M_w/M_n = 1.70$). The vinyl group functionalization (^1H n.m.r.) was 74%.

Preparation of PDES-56 using allyllithium, cryptand [211] and allyldimethylchlorosilane

This polymerization was performed under high vacuum conditions using break–seal techniques. The reaction vessel consisted of a 500 ml flask onto which had been sealed four ampoules containing the monomer (35 g, 343 mmol of diethylsiloxane units), allyllithium (2.4 ml of a 0.3 M solution, 0.72 mmol), cryptand [211] (303 mg, 1.05 mmol) and allyldimethylchlorosilane (1 ml, 7.4 mmol in 10 ml of absolute toluene), respectively. Before sealing the monomer within the ampoule, it was dried azeotropically in toluene using dibutylmagnesium as the drying agent. The cryptand was dried by the same procedure before being sealed. Allyllithium and allyldimethylchlorosilane were degassed twice before being sealed.

The ring-opening polymerization was initiated by reaction of the monomer with allyllithium for 24 h at room temperature. Next, the cryptand was added to the slightly yellow reaction mixture and the polymerization was allowed to proceed for 8 h at room temperature, during which time the mixture turned into a brown-green viscous fluid. The propagation was stopped by addition of allyldimethylchlorosilane, at which instant the mixture decolorized. Termination was allowed to proceed for one week at room temperature before the vessel was opened. The crude polymeric product was purified by repeated precipitation in ethanol. The polymer yield was 31.1 g (89%) ($M_n = 56\,000\,g\,mol^{-1}$, $M_w/M_n = 1.27$). The vinyl group functionalization was ~ 85%.

Hydrosilylation crosslinking

Owing to the high viscosity of the PDES precursors, homogenization of the vinyl end-functionalized polymer, crosslinker and catalyst had to be performed in solution. Spin casting of the homogenized mixture into a dish-shaped mould allowed fast solvent evaporation, while the formation of gas bubbles could be prevented (*Figure 1*). Thus, 5 g of polymer was dissolved in 25 ml of absolute n-hexane, to which solution were added 1.5 equivalents of SiH units relative to the amount of vinyl or allyl groups and two drops of the platinum cyclovinylmethylsiloxane catalyst. The solution was filtered through a 0.45 μm filter to remove dust particles, and then slowly poured into the spinning mould (spinning rate 5000 rev min^{-1}) under an N_2 flow. To ensure easy release of the silicone rubber, the mould had previously been coated with a Teflon® film or a Kapton® polyimide film. The latter substrate was used to obtain rubbers with a smooth surface which could be used for birefringence measurements. Vulcanization was achieved by heating the spinning mould to 100°C for 2 h. After this procedure, the rubbers were removed from the mould and postcured under air at 110°C for 60 h. The dimensions of the rubber samples were $314 \times 15 \times 1\,mm^3$.

Methods

Gel permeation chromatography (g.p.c.) measurements were carried out in toluene as the solvent using Waters microstyragel columns (pore sizes of 10^5, 10^4, 10^3 and 10^6 Å). Molecular weights were determined by universal calibration based on narrowly dispersed polystyrene standards[19]. A dual detection system, consisting of a differential refractometer (Waters model 410) and a differential viscometer (Viscotek model H502, UNICAL software), allowed simultaneous determination of molecular weights, molecular weight distributions and intrinsic viscosities [η].

Solution ^1H n.m.r. spectra were recorded on a Bruker

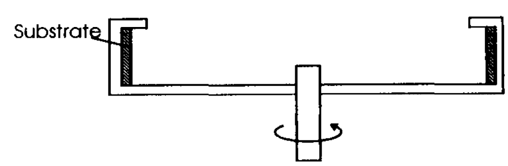

Figure 1 Schematic view of the mould

AC 250 spectrometer at 250.1 MHz with $CDCl_3$ as the solvent. The vinyl group content was estimated by means of an internal standard. For this purpose, an exactly known amount of polymer was dissolved in $CDCl_3$ which contained a known amount of dimethylformamide in the concentration range of the end-groups. The ratio of the dimethylformamide protons to the methyl protons of the chain stoppers at the chain ends yielded the number of end-groups. By measuring M_n via g.p.c. using universal calibration, the vinyl functionality could be calculated. For network precursors with $M_n >$ 50 000 g mol^{-1}, no reliable data could be obtained by this method. In this case, the degree of functionality may be estimated to be 80–90%. This estimation is justified by the fact that initiation with allyllithium yielded 50% vinyl functionalization. In addition, the termination reaction with allyldimethylchlorosilane was deliberately allowed to proceed for one week under rigorously purified conditions, during which time no decrease in viscosity was observed due to redistribution which would have indicated the presence of reactive silanolate end-groups.

A Perkin–Elmer DSC-2, modernized with regard to electronics and computer control, was used to monitor the thermal transitions at scan rates between 10 and 20 K min^{-1}. Cyclohexane was used as the calibration standard. Sample weights were typically chosen between 20 and 30 mg. The onset of the recorded endotherm on heating was taken as the transition temperature. Before the first heating scan, the samples were cooled from room temperature to 130 K at 10 K min^{-1}, annealed for 2 min and then heated at 20 K min^{-1} to 330 K. This procedure allowed investigation of the crystallization process under approximate equilibrium conditions. The second heating scan was recorded after cooling the sample from the amorphous state at 330 K to 130 K at 100 K min^{-1} which allowed consideration of the influence of chain ends or crosslinks on the kinetic phase formation. The crystallinity was estimated by comparison of the sum of the experimental PDES transition enthalpies with literature values reported for nearly 100% crystalline samples[12,13].

X-ray diffraction patterns were obtained using Ni-filtered CuKα radiation. Temperature dependent diffractograms were recorded on a circular film with a radius of 57.3 mm using a Guinier–Simon camera as described elsewhere[20]. Optical density data were collected from the photographically obtained patterns using a LS20 linear microdensitometer controlled by SCANPI software.

Sol fractions were determined by immersing ca. 0.25 g of a network sample in 25 ml toluene, which was refreshed every two days for a total period of two weeks. After this procedure, the samples were dried to constant weight. Sol fractions were calculated from the weight difference between the unextracted and extracted samples divided by the weight of the unextracted sample.

Equilibrium swelling of the networks was determined after two weeks of immersion in toluene from the weight increase due to absorption of toluene relative to the weight of the dry extracted sample.

RESULTS AND DISCUSSION

Cationic polymerization of hexaethylcyclotrisiloxane

The relative order of reactivity of siloxane bonds towards electrophilic attack follows the pattern $D_3 > MM > MDM > MD_2M > D_4$, in which the letters D and M refer to a diorgano- and a triorgano-substituted siloxane unit, respectively[21,22].

Besides the ring strain of ca. 15 kcal mol^{-1} (1 kcal = 4.2 kJ) present in the cyclic trimer, the reactivity is determined by the basicity of the oxygen atoms. This is normally highest for oxygen atoms surrounded by trialkyl-substituted silicon atoms like in MM, but it is also affected by the so-called $p\pi$–$d\pi$ effect, i.e. back-donation of the oxygen 'lone pair' electrons to the *d*-orbital of the adjacent silicon atom. In the strained trimer, less effective orbital overlap through bond angle distortion causes the $p\pi$–$d\pi$ effect to be smaller and results in a higher basicity of the oxygen atoms than in the case of unstrained siloxanes.

In the case of cationic polymerization of hexaethylcyclotrisiloxane in the presence of M_vM_v, the basicity of the oxygen atoms in the cyclic trimer is probably even higher than for the hexamethylcyclotrisiloxane owing to the slightly stronger electron-donating character of ethyl groups in comparison with methyl groups. Moreover, the presence of electron-withdrawing vinyl groups in M_vM_v may diminish the basicity of its oxygen atom compared to that of hexamethyldisiloxane. Hence, it can be expected that the end functionalization reaction during cationic polymerization of hexaethylcyclotrisiloxane in the presence of M_vM_v is slow relative to the propagation reaction. In order to enhance end functionalization, a molar ratio of 10 : 1 for the chain stopper relative to the initiator was employed. The molecular weights, polydispersities and vinyl functionalities of various network precursors thus prepared are presented in *Table 1*.

For polydiethylsiloxane telechelics of moderate molecular weight, i.e. $M_n > 25\,000$ g mol^{-1}, the calculated values for M_n and the experimentally determined values could be correlated, and the efficiency of vinyl functionalization was good. When the molecular weight exceeded 25 000 g mol^{-1}, the experimental molecular weights started to deviate severely from the calculated values, and also the extent of vinyl functionalization decreased. Long polymerization times and the use of only small amounts of initiator and chain stopper might have increased the influence of trace impurities. Chain transfer to water and the formation of silanol end-functionalized polydiethylsiloxane explain the lower molecular weights than theoretically calculated.

Anionic polymerization of hexaethylcyclotrisiloxane

Better control over the molecular weight could be

Table 1 Molecular weights, polydispersities, intrinsic viscosities and vinyl functionalities of various polydiethylsiloxane network precursors prepared by cationic polymerization

M_n [a] (g mol^{-1})	M_n [b] (g mol^{-1})	Yield (%)	M_w/M_n [b]	$[\eta]$ [b] (dl g^{-1})	VGF [c] (%)
10 000	13 080	76	1.70	0.076	100
25 000	22 000	80	1.70	0.163	74
50 000	28 700	78	1.80	0.211	52
100 000	43 270	73	1.87	0.296	39

[a] Calculated values
[b] Upon g.p.c. elution, according to universal calibration
[c] Vinyl group functionality according to ^{1}H n.m.r.

obtained through a 'living' anionic ring-opening polymerization of hexaethylcyclotrisiloxane with allyllithium in the presence of cryptand [211][23]. Initiation occurred upon addition of allyllithium to the cyclic monomer. The silanolate anions formed by ring opening of hexaethylcyclotrisiloxane are strongly bound to the lithium counterions and do not participate in the propagation reaction until addition of the cryptand [211], which solvates the lithium cations. In this manner, separation of the initiation and propagation reactions is achieved which helps to reduce the polydispersity of the resulting polymers (*Table 2*).

Hydrosilylation crosslinking

Crosslinking of vinyl end-functionalized network precursors was achieved by means of hydrosilylation of the terminal vinyl or allyl groups using an eight-functional SiH crosslinking agent in the presence of a catalytic amount of a platinum cyclovinylmethylsiloxane complex. A 1.5-fold molar excess of SiH groups relative to the maximum theoretical amount of vinyl or allyl groups was used. All components were mixed in n-hexane solution, followed by spin casting into a spinning mould which was subsequently heated to 100°C to effect vulcanization.

Results of sol fraction determinations and investigations on the equilibrium swelling behaviour in toluene are listed in *Table 3*. Before crosslinking, the PDES telechelics had all been purified by means of extraction. Therefore, it can be assumed that the sol fractions did not contain cyclic or linear oligomeric products, but consisted of polymeric meterial which had not been crosslinked. As all network precursors were subjected to the same crosslinking procedure, the sol fractions constitute a qualitative indication of the efficiency of the end functionalization and crosslinking reactions.

From *Table 3*, it appears that an increase in the molecular weight of the precursor was accompanied by an increase in the sol fraction. For the network precursors which had been prepared by means of cationic polymerization, the rather steep increase in the sol fraction is consistent with the strong decline in the functionalization efficiency shown by ^{1}H n.m.r. experiments.

Use of a functional initiator and consecutive deactivation of living chain ends with a functional end-capper yielded telechelic PDES samples with well-defined molecular weights and high end-group functionalities, as demonstrated by the sol fraction values. Higher sol fractions in the case of very high molecular weights do not necessarily reflect incomplete functionalization of the network precursors. The increase in sol fraction with molecular weight might also be due to incomplete conversion because of the decreased concentration of end-groups and diffusion limitations. Similar observations have been made during the hydrosilylation crosslinking of high molecular weight polydimethylsiloxane network precursors substituted with pendant vinyl groups[3].

Table 2 Molecular weights, polydispersities, intrinsic viscosities and vinyl functionalities of polydiethylsiloxane network precursors prepared by anionic polymerization

M_n [a] ($g\,mol^{-1}$)	M_n [b] ($g\,mol^{-1}$)	Yield (%)	M_w/M_n [b]	$[\eta]$ [b] ($dl\,g^{-1}$)	VGF [c] (%)
50000	56000	89	1.27	0.302	~85
100000	94000	94	1.55	0.452	~85
150000	115000	90	1.31	0.536	~85

[a] Calculated values
[b] Upon g.p.c. elution, according to universal calibration
[c] Vinyl group functionality, estimated

Table 3 Sol fractions and equilibrium swellings of polydiethylsiloxane networks prepared via hydrosilylation crosslinking of vinyl end-functionalized polydiethylsiloxane precursors

M_c ($g\,mol^{-1}$)	Sol fraction [a] (%)	Equilibrium swelling [b] (%)
Unimodal networks		
22000 [c]	11.7	364
29000 [c]	22.1	665
45000 [c]	31.6	1034
56000 [d]	12.0	587
94000 [d]	22.1	1077
115000 [d]	44.0	2195
Bimodal networks		
32000 [e]	11.0	440
49000 [f]	11.1	532

[a] Upon toluene extraction
[b] After 15 days of immersion in toluene at room temperature
[c] Precursor prepared via cationic polymerization
[d] Precursor prepared via anionic polymerization
[e] Average M_c for 50 wt% PDES-22 and 50 wt% PDES-56
[f] Average M_c for 10 wt% PDES-22 and 90 wt% PDES-56

Two bimodal networks were prepared by mixing of telechelic PDES samples with molecular weights of 22 000 and 56 000 $g\,mol^{-1}$ in weight ratios of 1:9 and 5:5. As with the respective unimodal networks, the bimodal networks also displayed low sol fractions.

The degree of swelling of the crosslinked PDES samples synthesized by anionic polymerization was almost 50% less than for the crosslinked samples prepared by cationic polymerization. This is consistent with a higher vinyl functionality.

In order to verify the network crosslink density and to estimate the Flory–Huggins polymer–solvent interaction parameter χ_1, equilibrium swelling data were evaluated by means of the Flory–Rehner equation[24]

$$-[\ln(1-v_2)+v_2+\chi_1 v_2^2] = V_1 n(v_2^{1/3} - 2v_2/f)$$

where v_2 is the volume fraction of the polymer in the swollen mass, V_1 is the molar volume of the solvent and f is the functionality at the crosslinks. Since the crosslinker had an average SiH content of eight groups per molecule and the ratio of SiH groups to vinyl groups was 1.5, the maximum functionality f at the crosslinks in the networks amounted to 5.3. Assuming complete end functionalization of the network precursor chains, the number of crosslinks per unit volume results from $n = 2\rho/fM_c$, where the polymer density[12,13] $\rho = 0.99\,g\,ml^{-1}$ for PDES in the amorphous phase and M_c is the molecular weight between crosslinks. Unreasonable values of 0.5–0.6 were obtained for the χ_1 parameter, i.e. higher than for a theta solvent ($\chi = 0.5$). This inconsistency demonstrates a significant deviation of the real network structure from the ideal one and might be explained in terms of dangling ends and a certain heterogeneity of the network structure due to incomplete end functionalization and/or incomplete conversion in the crosslinking reaction. A more reliable

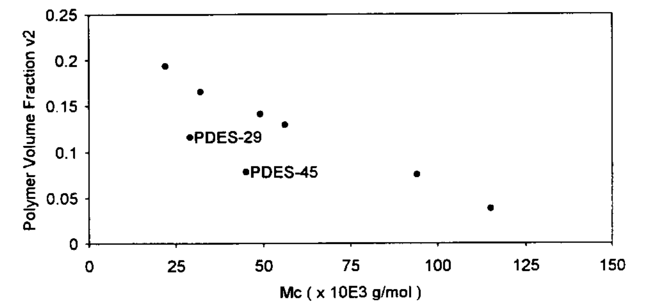

Figure 2 Polymer volume fraction in swollen polydiethylsiloxane networks as a function of M_c

evaluation of the network structure has to be based on an independent determination of χ_1.

Thermal behaviour

The vinyl-terminated PDES samples with M_n values of 22 000 g mol^{-1} (PDES-22), 56 000 g mol^{-1} (PDES-56), 94 000 g mol^{-1} (PDES-94) and 115 000 g mol^{-1} (PDES-115) and the corresponding unimodal and bimodal rubbers (10/90 PDES-22/PDES-56 and 50/50 PDES-22/PDES-56) were subjected to calorimetric measurements.

Figures 3a and *3b* depict the differential scanning calorimetry (d.s.c.) heating scans of the PDES-22 precursor and the PDES-22 network, respectively. Upper scans were recorded after cooling from the amorphous phase at 10 K min^{-1} to approach equilibrium conditions, whereas the lower scans were obtained after fast cooling from the amorphous phase at a rate of 100 K min^{-1} (kinetic control).

Heating a sample of the telechelic PDES-22 after slow cooling resulted in transitions with onset temperatures at 206 K and 273 K. These endotherms correspond to the α_1–α_2 and α_2–μ transitions reported elsewhere[12,13] and demonstrate predominant (70%) formation of the monoclinic α-crystal phase (*Figure 3a*). Small shoulders

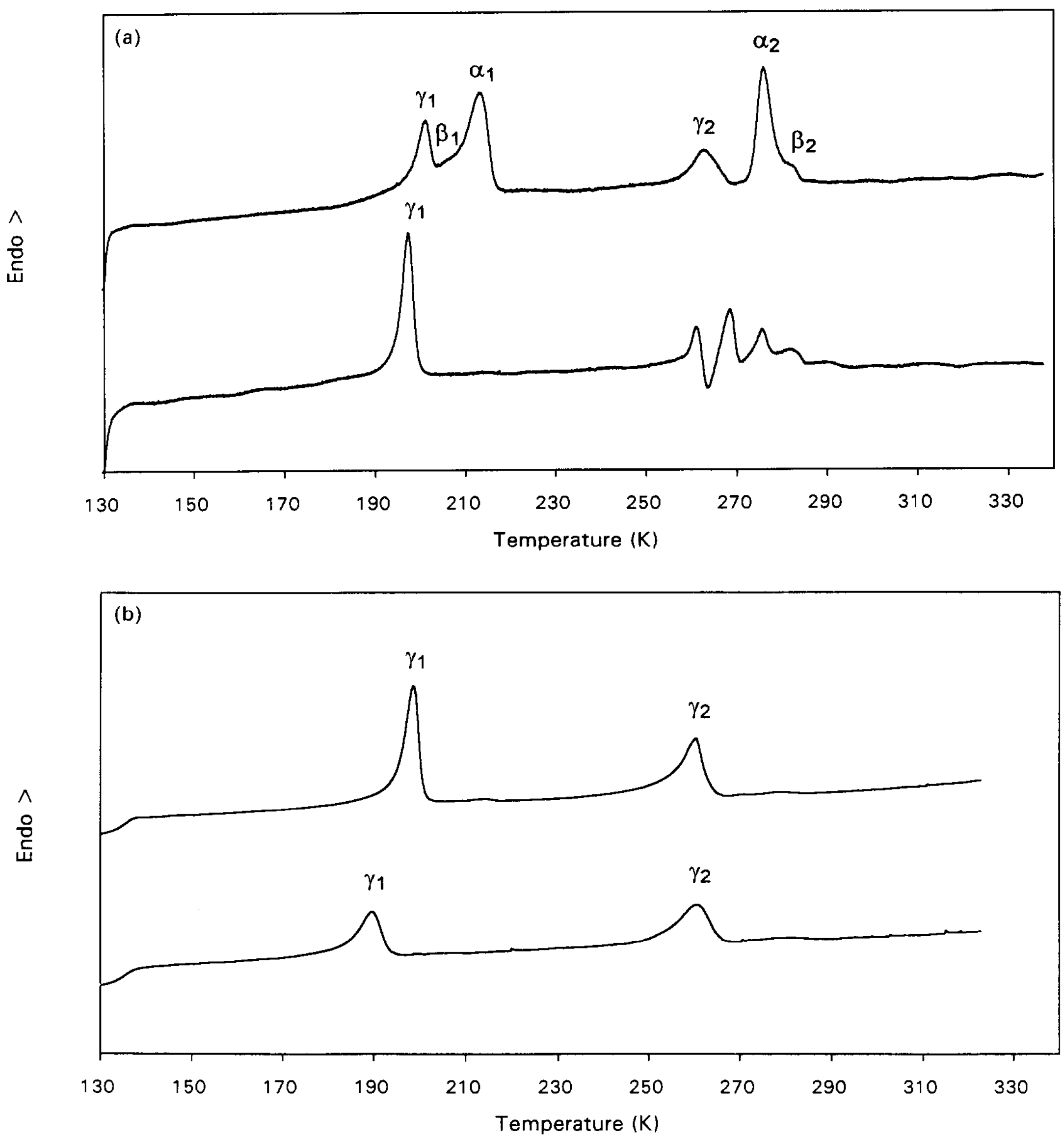

Figure 3 (a) D.s.c. heating scans of the polydiethylsiloxane precursor with M_n = 22 000 g mol^{-1} (rate 20 K min^{-1}). Before heating, the sample had been cooled at 10 K min^{-1} (top) or 100 K min^{-1} (bottom). (b) D.s.c. heating scans of the polydiethylsiloxane network with M_c = 22 000 g mol^{-1} (rate 20 K min^{-1}). Before heating, the sample had been cooled at 10 K min^{-1} (top) or 100 K min^{-1} (bottom)

at 202 K and 286 K correspond to the $\beta_1-\beta_2$ and $\beta_2-\mu$ transitions and indicate the formation of a minor amount of the tetragonal β-crystal modification. Additional transitions at 197 K and 257 K were denoted $\gamma_1-\gamma_2$ and $\gamma_2-\mu$ in order to distinguish them for the time being. The fraction of 'γ-crystalline' material was estimated to be 30%. No isotropization temperature was observed, indicating the inability of the PDES-22 sample to form a columnar mesophase[12,13]. Hence, melting of the α_2-phase or β_2-phase resulted in formation of the isotropic melt.

Fast cooling of the sample from the melt resulted in a markedly different d.s.c. heating trace. Both the $\alpha_1-\alpha_2$ and $\beta_1-\beta_2$ transitions disappeared, whereas the '$\gamma_1-\gamma_2$ transition' at 194 K remained. Further heating resulted in multiple melting transitions with peak temperatures at 264 K, 268 K, 275 K and 284 K. This remarkable multiple transition is not yet understood and will be the subject of further research. The first transition at 264 K might be correlated to melting of the 'γ_2-phase' followed by recrystallization into the α_2-phase. The transition at 284 K might be assigned to melting of the β_2-phase.

Slow cooling of the PDES-22 network from room temperature at 10 K min^{-1} resulted in the appearance of two 'γ-transitions' in the d.s.c. heating scan with onset temperatures at approximately 194 K and 253 K (*Figure 3b*). Fast cooling from 330 K resulted in the same transitions but also in a decrease in the transition enthalpies and a slight shift towards lower temperatures.

The pronounced glass transition at 136 K indicates that slow as well as fast cooling of the PDES-22 network resulted in significant glass formation. This is also reflected in the decreased heat of the endothermic transitions corresponding to degrees of crystallinity of 33% and 23% after slow and fast cooling, respectively. In contrast, the PDES-22 precursors showed 79% and 44% crystallinity after a similar thermal treatment.

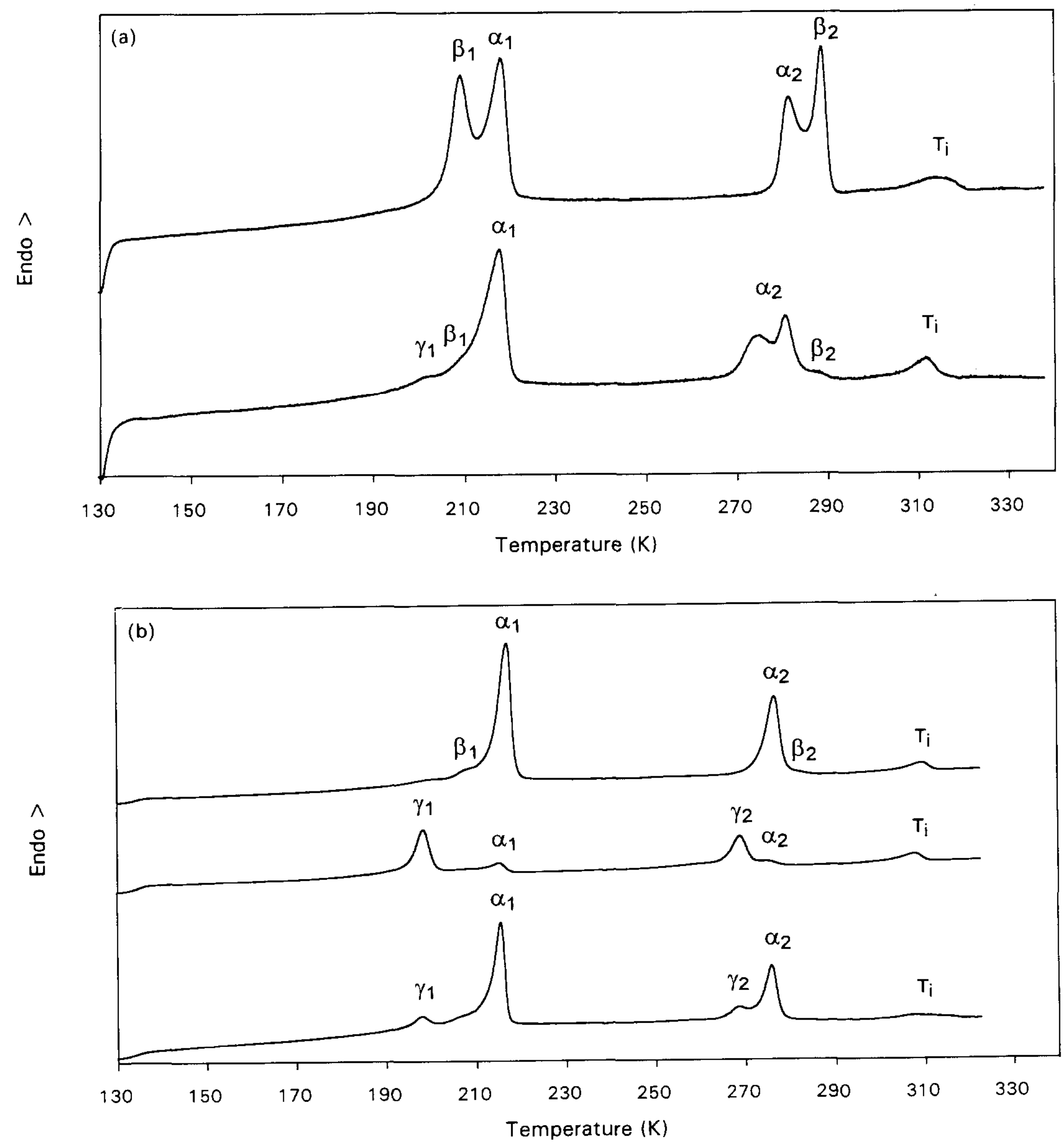

Figure 4 (a) D.s.c. heating scans of the polydiethylsiloxane precursor with $M_n = 94\,000$ g mol^{-1} (rate 20 K min^{-1}). Before heating, the sample had been cooled at 10 K min^{-1} (top) or 100 K min^{-1} (bottom). (b) D.s.c. heating scans of the polydiethylsiloxane network with $M_c = 94\,000$ g mol^{-1} (rate 20 K min^{-1}). Before heating, the sample had been cooled at 10 K min^{-1} (top) or 100 K min^{-1} (middle and bottom). The bottom d.s.c. scan was obtained on a stretched sample after cooling at 100 K min^{-1}

Upon increasing M_n with respect to M_c, the melting behaviour of the uncrosslinked and crosslinked materials became more similar. Regarding the temperatures of the observed transitions, all endotherms were originally assigned to the same transitions discussed so far, i.e. $\alpha_1-\alpha_2$ at an onset temperature of 206 K, α_2-μ at 273 K, $\beta_1-\beta_2$ at 202 K, $\beta_2-\mu$ at 286 K, $\gamma_1-\gamma_2$ at 197 K, $\gamma_2-\mu$ at 257 K and μ-isotropic melt at 280–330 K[12,13].

Figures 4a and *4b* depict the melting behaviour of the PDES-94 precursor and PDES-94 network, respectively. Slow cooling of the PDES-94 precursor from the mesophase at 293 K yielded the α-crystal and β-crystal modifications in approximate amounts of 60% and 40%, respectively (*Figure 4a*). In addition, the isotropization transition could be observed at 315 K. No formation of 'γ-crystalline' material was observed. Fast cooling from the isotropic melt at 330 K reduced the content of β-crystalline material to 10%, the remainder being α-crystalline material. The $\alpha_2-\mu$ transition showed two maxima which might hint at the formation of smaller and larger crystallites. The larger crystals might have been formed upon crystallization of the mesophase domains; the smaller ones by direct formation of α-phase crystallites from the isotropic melt.

Upon slow cooling of the PDES-94 network from room temperature, formation of the α-crystal and β-crystal modifications occurred in an approximate ratio of 95 : 5 (*Figure 4b*). In contrast, fast cooling from 330 K yielded 75% 'γ-crystalline' PDES, the remaining 25% being α-crystalline material. When the PDES-94 rubber was stretched at room temperature and then cooled rapidly from 330 K to 120 K, a reversal in the content of α-crystalline and 'γ-crystalline' material to approximately 90% α-phase and 10% 'γ-phase' was observed (*Figure 4b*). Hence, stretching seemed to favour formation of the α-crystalline modification relative to the 'γ-modification'.

Figure 5 depicts the degree of crystallinity as a function of the molecular weight for both precursors and networks upon slow and fast cooling. Crosslinks appeared to have a much stronger effect on the crystallization kinetics than end-groups. Under near-equilibrium conditions, however, the difference was smaller and became almost negligible in the case of low crosslink density. It may be noted that also the crystallinity of uncrosslinked PDES samples of high molecular weight decreased when they were cooled rapidly from the amorphous phase. This effect might be due to the presence of physical crosslinks, e.g. entanglements.

Figure 6 depicts the dependence of the isotropization temperature on the molecular weight for PDES precursors and networks. Both types of materials showed comparable isotropization temperatures upon slow cooling and upon quenching, although the values in the latter case were somewhat lower owing to the smaller size of the mesomorphic domains. When plotted against the reciprocal molecular weight, extrapolation to zero yielded $T_i = 330$ K for PDES networks with infinite molecular weight M_c, which is similar to observations reported elsewhere for linear uncrosslinked PDES (*Figure 7*)[14].

The question remains of whether the 'γ-transitions' indicate the formation of a new phase or whether the lower transition temperatures compared to the α-transitions and β-transitions indicate the formation of a fraction of smaller crystallites.

Figure 8 depicts the temperature dependent wide angle X-ray diffraction (WAXD) patterns of the PDES-22, PDES-56 and PDES-94 rubbers. The thermal history of the samples was similar to that in the slow cooling procedure used in the d.s.c. experiments. Thus, the PDES-22 rubber formed predominantly the 'γ-modification'. At 168 K, the PDES-22 rubber crystallized in a tetragonal crystal lattice with $a = 7.87$ Å and $c = 4.72$ Å (1 Å = 0.1 nm). Upon transition to the high temperature

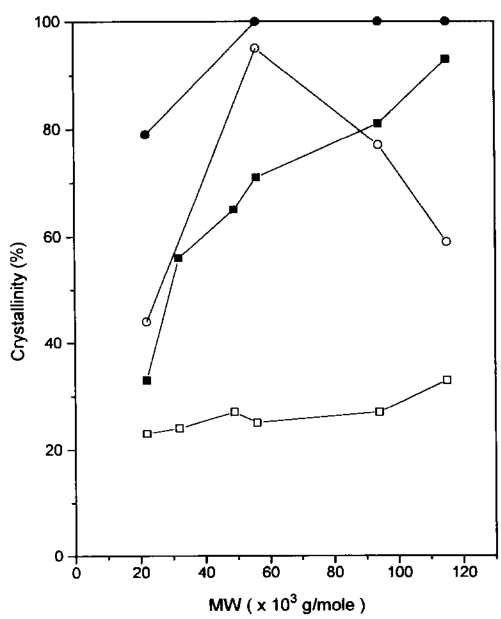

Figure 5 Crystallinity of networks (□, ■) and precursors (○, ●) under equilibrium (■, ●) and kinetic (□, ○) crystallization conditions as a function of molecular weight

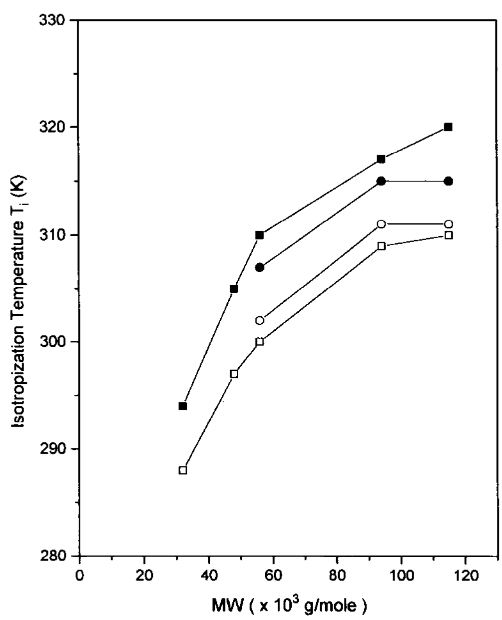

Figure 6 Molecular weight dependence of the isotropization temperature displayed by polydiethylsiloxane networks (□, ■) and precursors (○, ●) under equilibrium (■, ●) and kinetic (□, ○) crystallization conditions

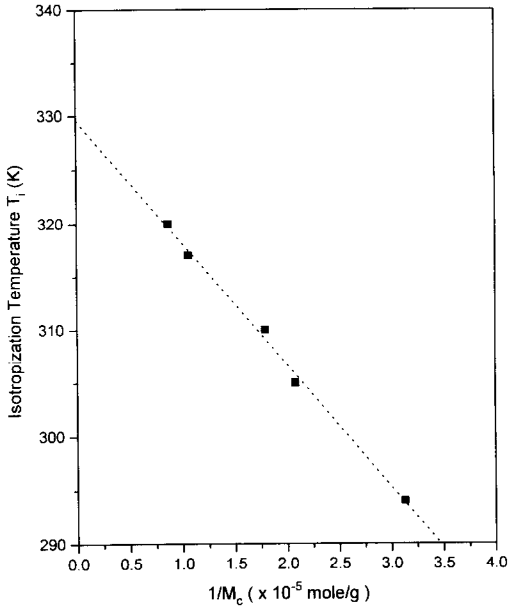

Figure 7 Isotropization temperature of polydiethylsiloxane networks as a function of the reciprocal molecular weight between crosslinks

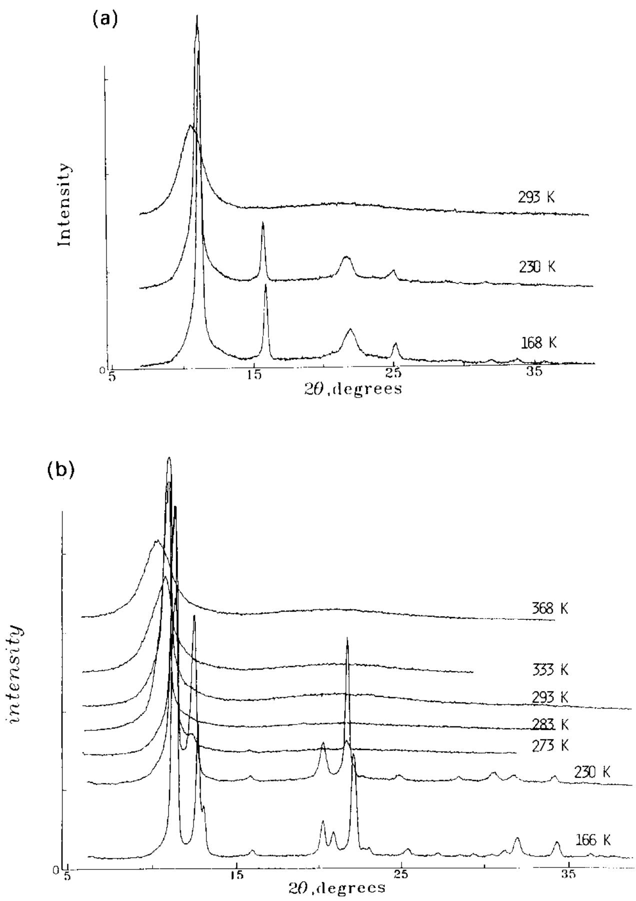

Figure 8 Temperature dependent WAXD patterns of polydiethylsiloxane networks with different M_c values: (a) 22 000 g mol^{-1}; (b) 94 000 g mol^{-1}.

crystal phase, the symmetry of the crystal lattice remained tetragonal but the *a* parameter changed to 7.92 Å. Consistent with the d.s.c. results, the rubber is completely amorphous at 293 K.

The 'γ-crystal modification' shown in *Figure 8a* appeared to be highly ordered and closely resembled the β-crystal modification displayed by high molecular weight PDES samples which had been slowly cooled from the columnar mesophase[12,13]. In fact, the *a* parameter of the unit cell of 'γ_1-crystalline' PDES was only 0.05 Å longer than the *a* parameter of the tetragonal unit cell of β_1-PDES, which is within experimental error.

Comparison of the WAXD pattern of the PDES-94 rubber at 166 K with that of the PDES-22 rubber revealed that PDES-94 contains two crystal modifications, i.e. a small amount of tetragonal β-crystalline material and a large fraction of monoclinic α-crystalline material. At 273 K only the reflections of the thermodynamically stable tetragonal modification were visible, which is consistent with the d.s.c. observations. Beyond 273 K the diffractogram showed two reflections which could be correlated to the 100 and 110 reflections of the hexagonal columnar phase. At 333 K the PDES-94 rubber transformed into an amorphous material.

Temperature dependent WAXD investigations of the PDES-56 rubber at 273 K demonstrated that the amorphous scattering of the polysiloxane chains is superimposed by a small but sharp reflection corresponding to the 100 reflection of the columnar mesophase. This observation hinted at the presence of mesomorphic domains in an amorphous matrix. Above 303 K the mesomorphic domains melted and the rubber became completely amorphous.

CONCLUSIONS

Hydrosilylation crosslinking of vinyl end-functionalized PDES precursors of various molecular weights provides a method of preparing model networks differing in thermal behaviour. The PDES precursors and the networks showed comparable phase behaviour, with the formation of α-crystal, β-crystal and 'γ-crystal' modifications. The thermodynamic stability of these three modifications followed the pattern 'γ' < α < β. Temperature dependent WAXD measurements indicated that the 'γ-transitions' were derived from melting of a tetragonal crystal modification with similar unit cell dimensions to β-crystalline PDES.

The PDES precursors and the corresponding networks showed analogous isotropization temperatures, suggesting that crosslinks and chain ends have similar effects on the lamellar thickness of the mesophase crystallites.

Crosslinks appeared to have a significantly larger effect on the kinetic crystallinity than end-groups, but the difference at equilibrium crystallization appeared to be small, especially in the case of weakly crosslinked materials. For high molecular weight PDES telechelics, physical crosslinking led to a reduction in the kinetic crystallinity as well.

In order to correlate the different PDES crystal modifications observed so far, the following observations should be considered. The monoclinic α-modification might be regarded as an undercooled crystalline version of the PDES mesophase in which the extended but conformationally disordered polymer chains display a two-dimensional monoclinic ordering slightly different from pseudo-hexagonal packing[12,13]. The thermodynamically stable tetragonal β-modification is only formed upon slow cooling from the columnar mesophase and displays an extended chain morphology. The tetragonal 'γ-modification' is preferentially formed under constrained conditions upon fast cooling of amorphous PDES networks and telechelics. Stretching and fast cooling of networks with high M_c values resulted in transformation of 'γ-crystalline' PDES into monoclinic α-crystalline PDES. In view of the similar unit cell parameters of the β-phase and 'γ-phase', it might be proposed that the 'γ-modification' is similar to the β-modification but differs in the crystal size and possibly in the occurrence of chain folding.

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