The preparation and hydrosilylation crosslinking of well-defined vinyl and ally1 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. 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. A number of previous investigations have been directed towards networks based on polydiethylsiloxane (PDES) which exhibits a columnar mesophase. This peculiar mesomorphic behaviour is based on the conformational disordering of the polymer main chain and side groups. 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, 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.

Linear uncrosslinked PDES has been extensively investigated with regard to its melting behaviour. 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 (α1, α2 and β1, β2) which are separated by a first-order crystal–crystal transition. The α-crystal and β-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, 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-crystal modification upon crystallization of the network. 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. 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 ($D_3Et_3$) was prepared as described elsewhere, distilled from CaH$_2$ and subsequently kept under argon. Trifluoromethanesulfonic
acid (triflic acid, CF$_3$SO$_2$H) (Alfa) was freshly distilled under vacuum before its use as an initiator. Divinyltetramethyldisiloxane (M$_3$M$_6$) (Aldrich) was distilled from CaH$_2$. The SiH crosslinking agent, a branched hydrodiphenylsiloxane oligomer with the average formula [SiO$_2$]$_4$[Si(O$_2$)$_2$ (CH$_3$)$_2$]H$_6$ [10], the platinum cyclovinyldimethylsiloxane complex PC085 (Hüls), allyldimethylchlorosilane (Aldrich, 98%), allyltriphenyltin (Aldrich, 99%) and phenylmagnesium (Aldrich, 1.8 M in pentane/diethyl ether) were used as received. Kryptofix [21] (Aldrich) was distilled under high vacuum conditions to 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 Seylerth and Weiner [11] was followed. A 250 ml three-necked flask equipped with a stirring bar and argon inlet was charged with 25 g (0.063 mol) of allyltriphenyltin and 140 ml of absolute diethyl ether. To the resulting slightly turbid solution was slowly added 35.5 ml (0.63 mol) of 1.8 M phenylmagnesium 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 acetic acid/trifluoroacetic acid in dimethyl sulfoxide [18]. The solution was stored under argon at $-20°C$.

Preparation of PDES-22 using triflic acid and M$_3$M$_6$

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 ml (2.1 mmol) of M$_3$M$_6$ was added through the septum. The mixture was homogenized by stirring for 5 min, followed by addition of 19 ml (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 11 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$^{-1}$, $M_n$/M$_w$ = 1.70). The vinyl group functionalization ($^{1}HNMR$) was 74%.

Preparation of PDES-56 using allyllithium, cryptand [21] 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 (2.1 ml of a 0.3 M solution, 0.72 mmol), cryptand [21] (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$^{-1}$, $M_n$/M$_w$ = 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 cyclovinyldimethylsiloxane 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 x 15 x 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$^2$ 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 [9].

Solution $^1$HNMR spectra were recorded on a Bruker...
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\(^1\,\text{a}\,\text{b}\).

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 $\pi$-donor 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 $\pi$- donor 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,M, the basicity of the oxygen atoms in the cyclic trimer is probably even higher than for the hexaethylcyclotrisiloxane 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,M 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,M 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., $M_w > 25 000$ g mol\(^{-1}\), the calculated values for $M_w$ 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.


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

<table>
<thead>
<tr>
<th>$M_w$ (g mol(^{-1}))</th>
<th>$M_n$ (g mol(^{-1}))</th>
<th>Yield (%)</th>
<th>$M_w/M_n$</th>
<th>$\eta_v$ (dL g(^{-1}))</th>
<th>VG (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 000</td>
<td>13 080</td>
<td>76</td>
<td>1.70</td>
<td>0.076</td>
<td>100</td>
</tr>
<tr>
<td>25 000</td>
<td>22 000</td>
<td>80</td>
<td>1.70</td>
<td>0.163</td>
<td>74</td>
</tr>
<tr>
<td>50 000</td>
<td>28 700</td>
<td>78</td>
<td>1.80</td>
<td>0.211</td>
<td>52</td>
</tr>
<tr>
<td>100 000</td>
<td>43 270</td>
<td>73</td>
<td>1.87</td>
<td>0.296</td>
<td>39</td>
</tr>
</tbody>
</table>

\(^a\) 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 hexaethyldicyclosiloxane with allyllithium in the presence of cryptand [21][2]. Initiation occurred upon addition of allyllithium to the cyclic monomer. The silylamine anions formed by ring opening of hexaethyldicyclosiloxane are strongly bound to the lithium counterions and do not participate in the propagation reaction until addition of the cryptand [21], 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).

### Hydroisilillation crosslinking

Crosslinking of vinyl end-functionalized network precursors was achieved by means of hydroisilylation 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 material 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 1H 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 hydroisilylation crosslinking of high molecular weight polydimethylsiloxane network precursors substituted with pendant vinyl groups.

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 3:5. 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 $\chi_1$, equilibrium swelling data were evaluated by means of the Flory–Rehner equation

$$-\ln(1 - v_2) + v_2 + \chi_1v_2^2 = V_1n(v_2^{1/2} - 2v_2/f)$$

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 is consistent with the strong decline in the functionalization efficiency shown by 1H n.m.r. experiments.

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

<table>
<thead>
<tr>
<th>$M_a$ (g mol$^{-1}$)</th>
<th>$M_p$ (g mol$^{-1}$)</th>
<th>Yield (%)</th>
<th>$M_w/M_a$</th>
<th>$[\eta]$ (dl g$^{-1}$)</th>
<th>VGF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 000</td>
<td>56 000</td>
<td>89</td>
<td>1.27</td>
<td>0.302</td>
<td>~85</td>
</tr>
<tr>
<td>100 000</td>
<td>94 000</td>
<td>94</td>
<td>1.55</td>
<td>0.452</td>
<td>~85</td>
</tr>
<tr>
<td>150 000</td>
<td>115 000</td>
<td>90</td>
<td>1.31</td>
<td>0.536</td>
<td>~85</td>
</tr>
</tbody>
</table>

* Calculated values
* Upon g.p.c. elution, according to universal calibration
* Vinyl group functionality, estimated

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

<table>
<thead>
<tr>
<th>$M_c$ (g mol$^{-1}$)</th>
<th>Sol fraction (%)</th>
<th>Equilibrium swelling (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unimodal networks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22 000</td>
<td>11.7</td>
<td>364</td>
</tr>
<tr>
<td>29 000</td>
<td>22.1</td>
<td>665</td>
</tr>
<tr>
<td>45 000</td>
<td>31.6</td>
<td>1034</td>
</tr>
<tr>
<td>56 000</td>
<td>12.0</td>
<td>587</td>
</tr>
<tr>
<td>91 000</td>
<td>22.1</td>
<td>1077</td>
</tr>
<tr>
<td>115 000</td>
<td>44.0</td>
<td>2195</td>
</tr>
<tr>
<td>Bimodal networks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32 000</td>
<td>11.0</td>
<td>440</td>
</tr>
<tr>
<td>49 000</td>
<td>11.1</td>
<td>532</td>
</tr>
</tbody>
</table>

* Upon toluene extraction
* After 15 days of immersion in toluene at room temperature
* Precursor prepared via cationic polymerization
* Average $M_c$ for 50 wt% PDES-22 and 50 wt% PDES-56
* Average $M_c$ for 10 wt% PDES 22 and 90 wt% PDES 56

For further details, see the full text of the research article.
evaluation of the network structure has to be based on an independent determination of $\chi_1$.

**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 $\alpha_1-\alpha_2$ and $\alpha_2-\mu$ transitions reported elsewhere$^{12,13}$ and demonstrate predominant (70%) formation of the monoclinic $\alpha$-crystal phase (Figure 3a). Small shoulders
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 $\beta$-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 '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. Hence, melting of the $\alpha_2$-phase or $\beta_2$-phase resulted in formation of the isotropic melt.

Fast cooling of the sample from the melt resulted in a markedly different DSC 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 $\gamma_2$-phase followed by recrystallization into the $\alpha_2$-phase. The transition at 284 K might be assigned to melting of the $\beta_2$-phase.

Slow cooling of the PDES-22 network from room temperature at 10 K min$^{-1}$ resulted in the appearance of two 'crystalline' transitions' in the DSC 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) DSC heating scans of the polydiethylsiloxane precursor with $M_n = 94000$ 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) DSC heating scans of the polydiethylsiloxane network with $M_n = 94000$ 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 DSC scan was obtained on a stretched sample after cooling at 100 K min$^{-1}$.
Upon increasing $M$, with respect to $M_i$, 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, $\alpha_2 - \mu$ 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 $\mu$-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 $\alpha$-crystal and $P$-crystal modifications in approximate amounts of 60% and 40%, respectively (Figure 4a). In addition, the isotropization transition could be observed at 315K. No formation of $\gamma$-crystalline material was observed. Fast cooling from the isotropic melt at 330 K reduced the content of $\beta$-crystalline material to 10%, the remainder being $\alpha$-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 $\alpha$-phase crystallites from the isotropic melt.

Upon slow cooling of the PDES-94 network from room temperature, formation of the $\alpha$-crystal and $\beta$-crystal modifications occurred in an approximate ratio of 95:5 (Figure 4b). In contrast, fast cooling from 330 K yielded 75% $\gamma$-crystalline PDES, the remaining 25% being $\alpha$-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 $\alpha$-crystalline and $P$-crystalline material to 90% $\alpha$-phase and 10% $\gamma$-phase was observed (Figure 4b). Hence, stretching seemed to favour formation of the $\alpha$-crystalline modification relative to the $\gamma$-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 $M_\infty$, which is similar to observations reported elsewhere for linear uncrosslinked PDES (Figure 7).

The question remains of whether the $\gamma$-transitions indicate the formation of a new phase or whether the lower transition temperatures compared to the $\alpha$-transitions and $\beta$-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 $\gamma$-modification. At 168 K, the PDES-22 rubber crystallized in a tetragonal crystal lattice with $a = 7.87 \text{ Å}$ and $c = 4.72 \text{ Å}$ (1 Å = 0.1 nm). Upon transition to the high temperature
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 \( \gamma < \alpha < \beta \). 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. The thermodynamically stable tetragonal \( \beta \)-modification is only formed upon slow cooling from the columnar mesophase and displays an extended chain morphology. The tetragonal \( \gamma \)-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 \( \gamma \)-crystalline PDES into monoclinic \( \alpha \)-crystalline PDES. In view of the similar unit cell parameters of the P-phase and \( \gamma \)-phase, it might be proposed that the \( \gamma \)-modification is similar to the \( \beta \)-modification but differs in the crystal size and possibly in the occurrence of chain folding.

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