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# Preparation of highly thermally stable and soluble ethylene-crosslinked ladder-like polymethylsiloxanes *via* template polymerisation†

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In this study, ethylene-crosslinked ladder-like polymethylsiloxanes were prepared to achieve high polymer thermal stability and solubility. First, polysiloxane with diethoxymethylsilyl groups in its side chains was prepared *via* hydrosilylation between diethoxymethylsilane and polymethylvinylsiloxane. This polymer was then diluted in a mixed solvent of toluene and *N,N*-dimethylformamide (3:2, v/v). Subsequently, intramolecular polycondensation (template polymerisation) of the diethoxymethylsilyl groups was performed using purified water and hydrochloric acid as catalysts, affording ethylene-crosslinked ladder-like polymethylsiloxane (ECL-LPMS). Additionally, ECL-LPMS with trimethylsilyl-protected silanol groups (ECL-LPMS-TMS) was prepared by reacting the residual silanol groups in ECL-LPMS with chlorotrimethylsilane. Both polymers were soluble in various organic solvents. Solubility tests, gel permeation chromatography analysis, proton and silicon nuclear magnetic resonance spectroscopy, transmission electron microscopy and wide-angle X-ray diffraction measurement confirmed that the polymers featured a ladder-like structure comprising two polymethylsiloxane chains interconnected by ethylene linkages. Thermogravimetric analysis revealed high thermal stability, with 10% weight loss temperatures of 528 °C and 520 °C and residual weights of 81% and 65% at 800 °C for ECL-LPMS and ECL-LPMS-TMS, respectively. Ultraviolet–visible spectra of ECL-LPMS and ECL-LPMS-TMS cast films exhibited over 90% transmittance across a wide wavelength range (250–800 nm), indicating excellent transparency.

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## Introduction

One primary limitation of conventional polymer materials is their tendency to degrade when exposed to heat and ultraviolet (UV) light. Such degradation begins with the abstraction of hydrogen atoms, ultimately leading to the formation of carbon radicals under the influence of heat and light energy. This process deteriorates mechanical properties and causes decolorisation owing to progressive molecular cleavage.<sup>1,2</sup> However, some polymer materials, namely aromatic polyimides, fluoropolymers (*e.g.*, poly(tetrafluoroethylene)) and silicones (*e.g.*,

polydimethylsiloxane), exhibit excellent resistance to heat, UV light and chemical degradation. Despite this, aromatic polyimides are prone to degradation as their transmittance deteriorates owing to UV-induced coloration.<sup>3</sup> Additionally, fluoropolymers encounter potential production restrictions owing to the formation of organofluorine compounds (*e.g.*, perfluorooctanoic acid and perfluorooctane sulfonic acid) during manufacturing.<sup>4</sup> Furthermore, the siloxane bonds in the main chain of silicones render them highly flexible, making them unsuitable for use as hard coating materials. Given these limitations of polymer materials, future developments aimed at applications in high-performance optoelectronics and other practical industrial uses are expected to focus on polymers that combine heat resistance, UV resistance, transparency, safety and hard coating properties, along with solubility—a feature not found in pure inorganic materials such as glass and ceramics.

Building on this background, the preparation of ladder-like polymethylsilsequioxane (PMSQ), characterized by a low organic content (*e.g.*, methyl side chains), has been investigated for its heat and UV resistance. However, synthesising ladder-like PMSQ directly from trifunctional silane coupling agents (*e.g.*, trichloromethylsilane and trialkoxymethylsilane),

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commonly used as starting materials, is challenging. Notably, the sol-gel reaction of these silane coupling agents generally produces random, disordered structures, and efforts to synthesise high-molecular-weight materials often lead to insoluble network structures. To address these challenges, reported methods involve the prior synthesis of *cis-trans-cis* cyclic tetrasiloxane precursors with reactive groups, followed by polycondensation.<sup>5–7</sup> Polymers prepared *via* these methods exhibit high thermal resistance, with thermal decomposition temperatures (10% weight loss temperature,  $T_{d10}$ ) exceeding 500 °C. However, these methods rely on cyclic tetrasiloxane precursors obtained through complex multistep processes, posing challenges for large-scale production.

In a previous study, we reported the preparation of ladder-like polysilsesquioxanes (PSQs) with ionic substituents, including ammonium,<sup>8–10</sup> carboxylate (carboxy),<sup>11</sup> sulfonate (sulfo)<sup>12</sup> and phosphonate (phosphonic acid) groups,<sup>13</sup> in their side chains through the hydrolytic polycondensation (sol-gel reaction) of trifunctional silane coupling agents. To improve the thermal stability of an ammonium-functionalised ladder-like PSQ, side-chain modifications with phthalic anhydride and benzoyl chloride were performed, yielding ladder-like PSQs with phthalimide and benzamide side groups and  $T_{d10}$  values of *ca.* 420 °C–440 °C.<sup>14,15</sup>

Additionally, we introduced a diethoxymethylsilyl group as a polymerisable unit into the side chains of a polysiloxane with 3-aminopropyl hydrochloride salt side chains,<sup>16</sup> followed by intramolecular polycondensation (template polymerisation), producing an alkyl-urea-crosslinked ladder-like polymethylsiloxane (AUCL-LPMS).<sup>17</sup> This polymer exhibited a  $T_{d10}$  value of 407 °C, demonstrating its relatively high thermal stability. In comparison, the  $T_{d10}$  values of the ammonium-functionalised single-chain polysiloxane (starting material) and the single-chain polysiloxane with alkyl urea side chains were 357 °C and 265 °C, respectively, indicating their lower thermal stability than the double-chain ladder-like polysiloxane. These findings demonstrate that the ladder-like structure with double main chains enhances thermal stability.

Thus, ladder-like siloxane polymers exhibit high thermal stability while retaining solubility. However, these polymers contain substantial organic components in their side chains (*e.g.*, phthalimide<sup>14</sup> and benzamide<sup>15</sup> in ladder-like PSQ) and crosslinking chains (*e.g.*, AUCL-LPMS<sup>17</sup>), limiting their  $T_{d10}$  values to below 500 °C. To address this, in the current study, we developed a new soluble ladder-like polysiloxane with enhanced thermal stability by reducing the organic content in the crosslinking chains of AUCL-LPMS. Similar to the thermally stable ladder-like PMSQ, this polymer features methyl groups in its side chains, with the two siloxane main chains linked *via* an ethylene chain instead of the oxygen atoms present in PMSQ.

Several methods for preparing ladder-like polymers have been established in previous research. For instance, the sol-gel reaction is commonly employed to prepare ladder-like PSQs,<sup>8–13,18–23</sup> whereas template polymerisation is widely used for ladder-like organic polymers. In template polymerisation,

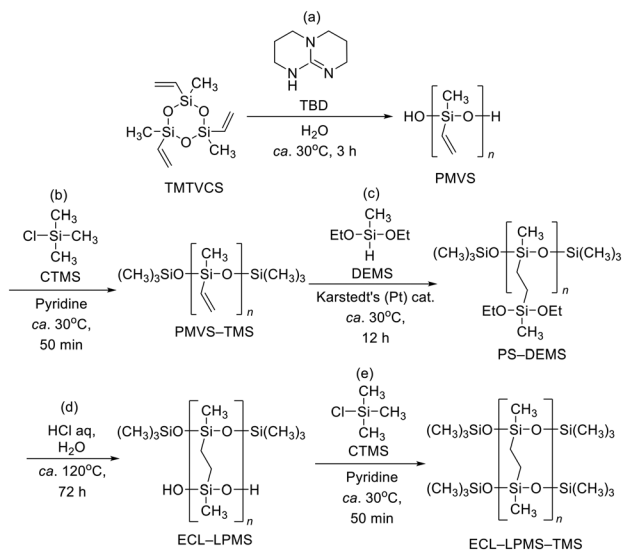
chain polymerisation methods, such as radical polymerisation, are particularly prominent. For instance, ladder-like polymers have been prepared through the intramolecular radical polymerisation of *p*-cresol oligomers containing acrylic groups,<sup>24,25</sup> along with multivinyl polymers derived from polyvinyl alcohol<sup>26</sup> and poly(meth)acrylates.<sup>27–32</sup> Template polymerisation in step-growth systems, similar to the method used for AUCL-LPMS, has also been reported. Using this approach, we recently prepared an amphiphilic ladder-like polymer composed of a hydrophilic polyether chain and a hydrophobic polysiloxane chain.<sup>33</sup>

In the present study, we prepared ladder-like polysiloxanes with methyl side chains and ethylene crosslinking chains, hypothesizing that the rigidity provided by the unique double-chain structure and minimal organic content would enhance thermal stability. Additionally, the one-dimensional ladder-like structure demonstrated good solubility. Polymethylsiloxane with diethoxymethylsilyl groups linked *via* ethylene in its side chains underwent template polymerisation in a dilute solution. The resulting ladder-like polysiloxanes were soluble in various organic solvents and exhibited a  $T_{d10}$  value exceeding 500 °C. Films cast from these polymers were colourless and transparent, with high transmittance (over 90%) across the 250–800 nm UV-visible (UV-Vis) range.

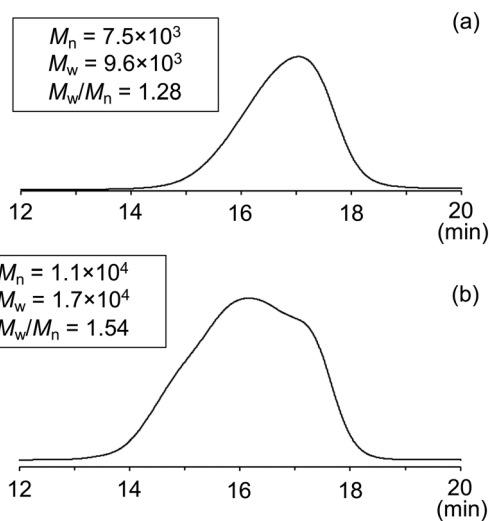
## Results and discussion

### Preparation of ethylene-crosslinked ladder-like polymethylsiloxanes (ECL-LPMS and ECL-LPMS-TMS)

Ethylene-crosslinked ladder-like polymethylsiloxanes with unprotected silanol groups (ECL-LPMS) were prepared through two steps: hydrosilylation between diethoxymethylsilane (DEMS) and polymethylvinylsiloxane terminated with trimethylsilyl groups (PMVS-TMS, Schemes 1a and b, and Fig. 1a, 2a and 3a),<sup>34</sup> followed by template polymerisation of the diethoxymethylsilyl groups in the side chains of the polymer. First, hydrosilylation between DEMS and PMVS-TMS (weight-average molecular weight ( $M_w$ ) =  $9.6 \times 10^3$ , molecular weight distribution ( $M_w/M_n$ ) = 1.28) was performed using a platinum (0)-1,3-divinyltetramethyldisiloxane complex catalyst (Karstedt's catalyst) in dehydrated xylene (a commercial mixture containing *ca.* 80% *o*-, *m*- and *p*-xylene and *ca.* 20% ethylbenzene). The reaction produced polymethylsiloxane with diethoxymethylsilyl groups linked *via* ethylene bridges in its side chains (PS-DEMS, Scheme 1c). To assess the progress of hydrosilylation, the solid product was isolated by reprecipitation; however, solubility tests confirmed that it was insoluble in all tested solvents. Hence, once the reaction was completed, a mixed toluene : *N,N*-dimethylformamide (DMF) (3 : 2, v/v) solvent was added directly to the reaction solution, without product isolation, to prepare a diluted solution ( $1.6 \times 10^{-3}$  mol unit per L). To ensure that the diethoxymethylsilyl groups in the PS-DEMS side chains reacted intramolecularly rather than intermolecularly, maintaining a low solution concentration during polycondensation was essential.

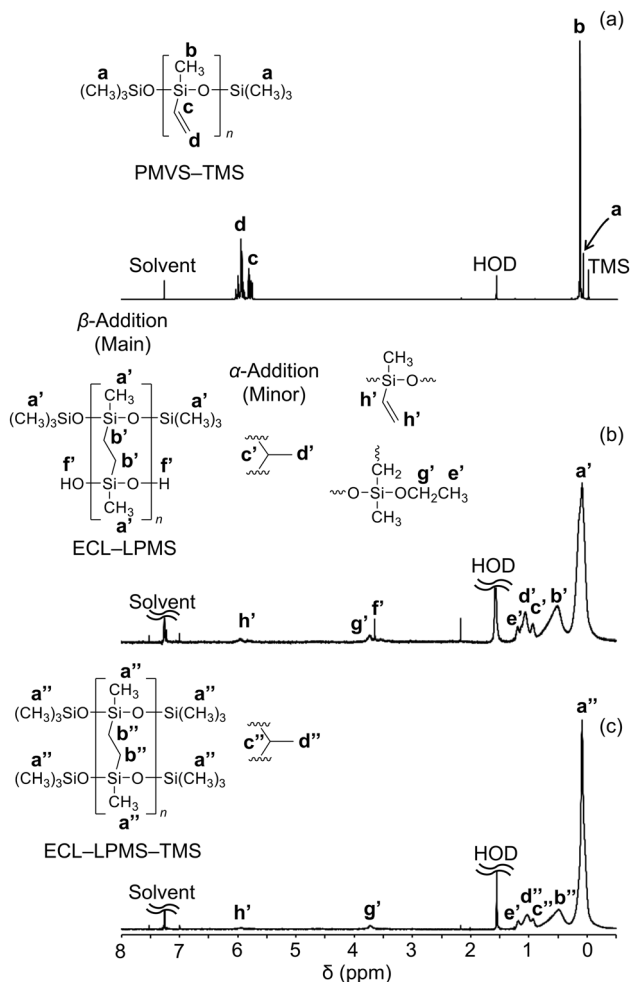


**Scheme 1** Preparation of (a) polymethylvinylsiloxane (PMVS) with unprotected silanol groups, (b) PMVS with trimethylsilyl-protected silanol groups (PMVS-TMS), (c) polymethylsiloxane with diethoxymethylsilyl groups linked via ethylene in its side chains (PS-DEMS), (d) ethylene-crosslinked ladder-like polymethylsiloxane with unprotected silanol groups (ECL-LPMS) and (e) ethylene-crosslinked ladder-like polymethylsiloxane with trimethylsilyl-protected silanol groups (ECL-LPMS-TMS).



**Fig. 1** GPC curves of (a) PMVS-TMS and (b) ECL-LPMS-TMS. Concentration: 0.5 w/v%, eluent: THF, standard: polystyrene.

Template polymerisation of the diethoxymethylsilyl groups in PS-DEMS was performed by adding purified water and concentrated hydrochloric acid, followed by stirring at 120 °C for 72 h (Scheme 1d). The reaction solution was concentrated using a rotary evaporator, and the product was reprecipitated from water to isolate it. For further purification, the water-insoluble fraction was collected by filtration. Methanol was then added to the water-insoluble portion to recover its soluble



**Fig. 2**  $^1\text{H}$  NMR spectra of (a) PMVS-TMS, (b) ECL-LPMS and (c) ECL-LPMS-TMS in  $\text{CDCl}_3$ . Chemical shifts are referenced to TMS ( $\delta$  0.0) for (a) and  $\text{CDCl}_3$  ( $\delta$  7.26) for (b) and (c).

portion, which was subsequently reprecipitated from water. The water-insoluble fraction was treated with *n*-hexane, and the resulting insoluble portion was collected as ECL-LPMS.

ECL-LPMS-TMS was prepared by reacting the residual silanol groups in ECL-LPMS with chlorotrimethylsilane (CTMS) in the presence of pyridine as a catalyst for protection (Scheme 1e). The chloroform solution of ECL-LPMS-TMS was reprecipitated from acetonitrile for purification. The acetonitrile-insoluble fraction was collected by filtration, dried under reduced pressure and afforded pure ECL-LPMS-TMS.

ECL-LPMS was soluble in ethanol, acetone, diisobutyl ketone (DIBK), tetrahydrofuran (THF), chloroform, ethyl acetate and diethyl ether, but was insoluble in water, dimethyl sulfoxide (DMSO), DMF, methanol and *n*-hexane. It was also partially soluble in  $\text{C}_n\text{H}_{2n+1}\text{OH}$  ( $n = 3$  and 4) and toluene (Table 1). In contrast, ECL-LPMS-TMS lost solubility in  $\text{C}_n\text{H}_{2n+1}\text{OH}$  ( $n = 2-4$ ) and acetone, where ECL-LPMS was soluble, but became soluble in toluene and *n*-hexane (Table 1).

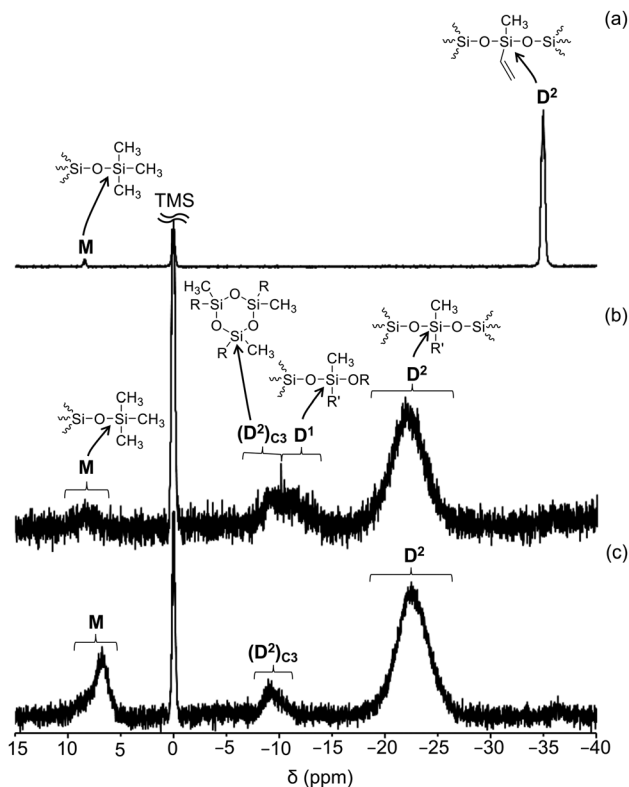


Fig. 3  $^{29}\text{Si}$  NMR spectra of (a) PMVS-TMS, (b) ECL-LPMS and (c) ECL-LPMS-TMS in  $\text{CDCl}_3$ . A small amount of  $\text{Cr}(\text{acac})_3$  was added as a relaxation agent. Chemical shifts are referenced to tetramethylsilane (TMS,  $\delta$  0.0).

### Structural analysis of ECL-LPMS and ECL-LPMS-TMS

Gel permeation chromatography (GPC), proton and silicon nuclear magnetic resonance ( $^1\text{H}$  and  $^{29}\text{Si}$  NMR) spectroscopy, transmission electron microscopy (TEM), wide-angle X-ray diffraction (WAXD) and solubility tests confirmed that ECL-LPMS-TMS possesses a ladder-like structure, with two polymethylsiloxane chains primarily linked by ethylene chains.

According to GPC measurements, the  $M_w$  and  $M_w/M_n$  values of the starting material PMVS-TMS were *ca.*  $9.6 \times 10^3$  and 1.28 (Fig. 1a), while those of the resulting polymer ECL-LPMS-TMS were  $1.7 \times 10^4$  and 1.54 (Fig. 1b), respectively. The higher  $M_w$  of ECL-LPMS-TMS compared to that of PMVS-TMS, along with the solubility test results, suggests minimal occurrence of intermolecular crosslinking reactions and successful intramolecular polycondensation.

The proportion of unreacted vinyl groups (5.95–5.79 ppm) remaining in the side chains of ECL-LPMS, calculated from the integral ratios of  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$ , was *ca.* 4.5% ( $[-\text{CH}=\text{CH}_2 \text{ (h'/3H)}]/[-\text{CH}_2\text{CH}_2- \text{ (b'/4H)}] + [-\text{CH}(\text{CH}_3)- \text{ ((c' + d')/4H)}] + [-\text{CH}=\text{CH}_2 \text{ (h'/3H)}]$ ), indicating that most of the vinyl groups had reacted (Fig. 2b). This result demonstrates the successful hydrosilylation between DEMS and PMVS-TMS. In addition, proton signals corresponding to unreacted ethoxy groups (3.73 and 1.19 ppm) and silanol groups (3.64 ppm)

Table 1 Solubility of ECL-LPMS and ECL-LPMS-TMS in various solvents

Product	Solubility <sup>a</sup>														
	Water	DMSO	DMF	DMF	MeOH	EtOH	$\text{C}_7\text{H}_{2n+1}\text{OH}$ ( $n = 3$ and 4)	$\text{Me}_2\text{CO}$	DIBK	THF	$\text{CHCl}_3$	Ethyl acetate	Diethyl ether	Toluene	<i>n</i> -Hexane
ECL-LPMS	-	-	-	-	-	+	+	+	+	+	+	+	+	+	+
ECL-LPMS-TMS	-	-	-	-	-	+	+	+	+	+	+	+	+	+	+

Abbreviations: DMSO: dimethylsulfoxide; DMF: *N,N*-dimethylformamide; MeOH: methanol; EtOH: ethanol;  $\text{C}_7\text{H}_{2n+1}\text{OH}$ : 1-propanol;  $\text{C}_3\text{H}_7\text{OH}$ : 1-butanol;  $\text{Me}_2\text{CO}$ : acetone; DIBK: diisobutyl ketone; THF: tetrahydrofuran;  $\text{CHCl}_3$ : chloroform. <sup>a</sup> Solubility: +: soluble at room temperature; -: insoluble at room temperature;  $\pm$ : partially soluble at room temperature.

were also detected (Fig. 2b). The proportions of ethoxy and silanol groups relative to the number of silicon atoms except trimethylsilyl groups were *ca.* 4.1%  $\{[-\text{SiOCH}_2\text{CH}_3 (g' \times 1\text{Si}/2\text{H})]/\{[-\text{SiCH}_2\text{CH}_2\text{Si-} (b' \times 2\text{Si}/4\text{H})] + [-\text{SiCH}(\text{CH}_3)\text{Si-} ((c' + d') \times 2\text{Si}/4\text{H})] + [-\text{SiCH}=\text{CH}_2 (h' \times 1\text{Si}/3\text{H})]\}\}$  and *ca.* 2.5%  $\{[-\text{SiOH} (f' \times 1\text{Si}/1\text{H})]/\{[-\text{SiCH}_2\text{CH}_2\text{Si-} (b' \times 2\text{Si}/4\text{H})] + [-\text{SiCH}(\text{CH}_3)\text{Si-} ((c' + d') \times 2\text{Si}/4\text{H})] + [-\text{SiCH}=\text{CH}_2 (h' \times 1\text{Si}/3\text{H})]\}\}$ , respectively, both of which were negligible. Furthermore, the molar ratio of the ethylene ( $\beta$ -addition) and methine ( $\alpha$ -addition) chains formed through hydrosilylation between DEMS and PMVS-TMS was determined to be 68 : 32 ( $b'/4\text{H} : (c' + d')/4\text{H}$ ), based on signals  $b'$  and  $(c' + d')$  in Fig. 2b.

Meanwhile, in the  $^1\text{H}$  NMR spectrum of ECL-LPMS-TMS in  $\text{CDCl}_3$  (Fig. 2c), the disappearance of silanol signals and the emergence of trimethylsilyl signals confirmed successful protection reaction with CTMS. The proportions of unreacted vinyl and ethoxy groups remaining in the side chains of ECL-LPMS-TMS were calculated using the same method as above to be *ca.* 3.8% and *ca.* 4.2%, respectively, showing similar values to those of ECL-LPMS. Additionally, the ethylene-to-methine chain ratio ( $71 : 29 = b''/4\text{H} : (c'' + d'')/4\text{H}$ ), based on signals  $b''$  and  $(c'' + d'')$  in Fig. 2c) was nearly identical to that of ECL-LPMS.

The  $^{29}\text{Si}$  NMR spectrum of ECL-LPMS in  $\text{CDCl}_3$  displayed a prominent signal in the  $\text{D}^2$  region ( $-26.5$  to  $-18.0$  ppm), a broad signal in the overlapping  $\text{D}^1$  and  $(\text{D}^2)_{\text{c}3}$  regions ( $-14.3$  to  $-7.1$  ppm),<sup>35</sup> and a minor signal in the M region (6.6 to 9.9 ppm), with an integral ratio of 80 : 18 : 2. No signal corresponding to the  $\text{D}^0$  structure was detected (Fig. 3b). This dominance of the  $\text{D}^2$  structure indicates that the polycondensation of the diethoxymethylsilyl groups in PS-DEMS proceeded adequately to form the second siloxane bond in the main chain.

Similarly, the  $^{29}\text{Si}$  NMR spectrum of ECL-LPMS-TMS in  $\text{CDCl}_3$  presented a prominent signal in the  $\text{D}^2$  region ( $-27.3$  to  $-18.8$  ppm) and two minor signals in the  $(\text{D}^2)_{\text{c}3}$  ( $-11.3$  to  $-7.5$  ppm) and M (4.9 to 9.7 ppm) regions, with an integral ratio of 82 : 3 : 15 (Fig. 3c). In the spectrum of ECL-LPMS, signals corresponding to the  $\text{D}^1$  and  $(\text{D}^2)_{\text{c}3}$  structures overlapped and broadened, whereas in the spectrum of ECL-PMS-TMS, this broadening was absent owing to the disappearance of the  $\text{D}^1$  structure, which occupies the upfield region of the signal. Moreover, the increased integral ratios of the  $\text{D}^2$  and M signals confirmed the successful protection of residual silanol groups in ECL-LPMS.

In the CTMS introduction reaction, the increase in the proportion of the M structure measured by  $^{29}\text{Si}$  NMR and the increase in the proportion of trimethylsilyl groups measured by  $^1\text{H}$  NMR were compared using their integral values. In the  $^{29}\text{Si}$  NMR spectrum (Fig. 3b and c), assuming that the total integral intensity of the signals attributed to the  $\text{D}^2$ ,  $(\text{D}^2)_{\text{c}3}$  and  $\text{D}^1$  structures is 100, the increase in the integral intensity of the M structure was 17.3% (21.8 for ECL-LPMS-TMS – 4.5 for ECL-LPMS). Meanwhile, in the  $^1\text{H}$  NMR spectra (Fig. 2b and c), assuming that the total number of silicon atoms corresponding to the repeating units  $[-\text{SiCH}_2\text{CH}_2\text{Si-} ((b' \text{ or } b'') \times 2\text{Si}/4\text{H})]$ ,  $[-\text{SiCH}(\text{CH}_3)\text{Si-} ((c' + d') \text{ or } (c'' + d'') \times 2\text{Si}/4\text{H})]$  and  $[-$

$\text{SiCH}=\text{CH}_2 (h' \times 1\text{Si}/3\text{H})]$  is 100, the increase in the proportion of trimethylsilyl groups  $[(a'' \text{ for ECL-LPMS-TMS} - a' \text{ for ECL-LPMS}) \times 1\text{Si}/9\text{H}]$  was calculated to be 16.4%. Therefore, the increase in the M structure (*i.e.*, trimethylsilyl groups) observed in both the  $^{29}\text{Si}$  and  $^1\text{H}$  NMR spectra was found to be nearly identical.

The TEM image of the sample prepared by drying an *n*-hexane solution of ECL-LPMS-TMS revealed a stripe pattern of parallel, linear molecules with a spacing of *ca.* 1.1 nm. This observation suggests that ECL-LPMS-TMS forms a one-dimensional polymer that aligns in a parallel (Fig. 4). Furthermore, WAXD measurements of ECL-LPMS-TMS confirmed weak diffraction peaks at  $q = 5.43 \text{ nm}^{-1}$ , indicating a periodic structure with an interval of *ca.* 1.1–1.2 nm (Fig. 5). The molecular dimension of a model compound representing the repeating unit of ECL-LPMS-TMS, subjected to energy minimization using the MM2 method in the CS Chem3D, was *ca.* 1.15 nm (Fig. 6). This value matches the molecular width of a single

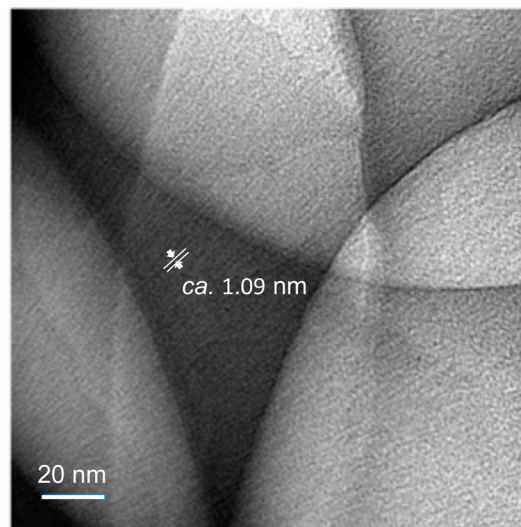


Fig. 4 TEM image of the sample obtained by drying an *n*-hexane solution of ECL-LPMS-TMS.

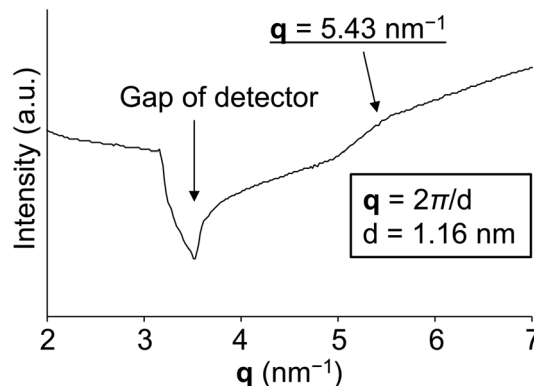


Fig. 5 WAXD line profile of ECL-LPMS-TMS.

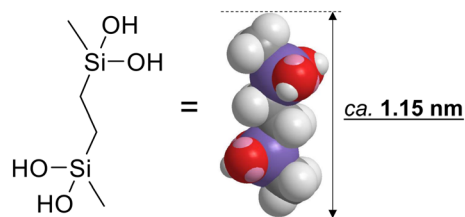


Fig. 6 Molecular dimensions of a model compound representing the repeating unit of ECL-LPMS-TMS, energy-minimized using MM2 in the CS Chem3D program package.

ECL-LPMS-TMS molecule and aligns with the 1.1–1.2 nm spacing observed in the TEM and WAXD results.

The structural analysis results of ECL-LPMS-TMS are summarised as follows. Solubility tests and GPC results indicated that ECL-LPMS-TMS is a polymer with minimal crosslinking. Its  $^1\text{H}$  NMR spectrum confirmed successful hydrosilylation between DEMS and PMVS-TMS. Further, its  $^{29}\text{Si}$  NMR results indicated that diethoxymethylsilyl groups attached to the first polysiloxane chain of PS-DEMS underwent polycondensation to form the second polysiloxane chains, although partial ring structures were also present. TEM and WAXD analyses revealed that ECL-LPMS-TMS exhibits a rigid one-dimensional structure. These findings indicate that ECL-LPMS-TMS features a ladder-like structure with two polysiloxane chains linked by ethylene chains, as illustrated in Fig. 7.

Template polymerisation at a higher concentration (10 times the original) instead of in a dilute solution produced a soluble polymer containing T structures ( $\text{RSi}(\text{OSi}\equiv)_3$ ). This suggests that at high concentrations, the polymerisation of diethoxymethylsilyl groups in the PS-DEMS side chains incorporated residual, unreacted DEMS that did not participate in the synthesis of PS-DEMS. Consequently, the second polysiloxane chain contained DEMS components. The hydrosilyl groups in the DEMS components were hydrolysed to form silanol groups, which then underwent dehydration condensation to form T structures (Fig. S1b $\dagger$ ). Owing to the relatively low proportion of T components, neither gelation nor insolubilization occurred.

### Thermal properties of ECL-LPMS and ECL-LPMS-TMS

Thermogravimetric analysis (TGA) of ECL-LPMS and ECL-LPMS-TMS was performed under nitrogen flow to assess their thermal stability. For comparison, an aromatic polyimide

(a known heat-resistant polymer) and methyl-containing siloxane compounds, including AUCL-LPMS,<sup>17</sup> polyhedral oligomeric silsesquioxane with methyl side-chains (Me-POSS) and a silicone membrane (Sylgard 184),<sup>36</sup> were also examined. The  $T_{\text{d}10}$  values of ECL-LPMS and ECL-LPMS-TMS were 528 °C and 520 °C, respectively (Fig. 8a and b), both exceeding 500 °C and comparable to the  $T_{\text{d}10}$  value of aromatic polyimide (Fig. S2a $\dagger$ ). Conversely, the  $T_{\text{d}10}$  values of other methyl-containing siloxane compounds were as follows: 407 °C for AUCL-LPMS (Fig. S2b $\dagger$ ), 250 °C for Me-POSS (Fig. S2c $\dagger$ ) and 444 °C for Sylgard 184 (Fig. S2d $\dagger$ ). All these values were lower than the  $T_{\text{d}10}$  values of ECL-LPMS and ECL-LPMS-TMS. Additionally, the residual weights of ECL-LPMS and ECL-LPMS-TMS at 800 °C were notably higher, at 81% and 65%, respectively (Fig. 8a and b), compared to the corresponding values of 47% for AUCL-LPMS (Fig. S2b $\dagger$ ), 0% for Me-POSS (Fig. S2c $\dagger$ ) and 28% for Sylgard 184 (Fig. S2d $\dagger$ ). The lower  $T_{\text{d}10}$  values and residual weights of AUCL-LPMS are likely attributed to its higher organic content. Similarly, Me-POSS exhibited lower thermal stability due to its low molecular weight, which promotes sublimation.<sup>37,38</sup> Sylgard 184 likely formed cyclic compounds during the decomposition of siloxane bonds upon heating,<sup>39</sup> resulting in evaporation. Meanwhile, the high thermal decomposition temperatures and residual weights of ECL-LPMS and ECL-LPMS-TMS are attributed to their low organic content, high molecular weight and unique double-chain structure, which enhance thermal stability.

Differential scanning calorimetry (DSC) measurements of PMVS-TMS (starting material) and ECL-LPMS-TMS were per-

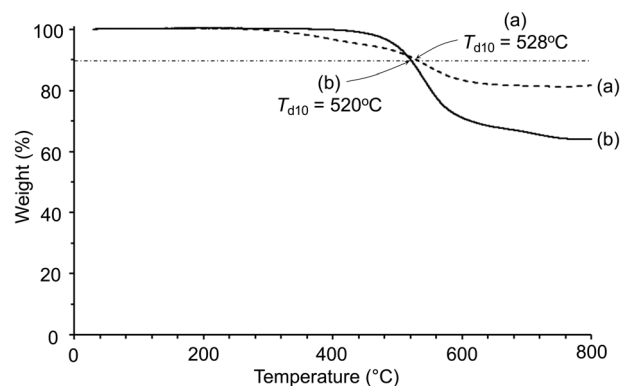


Fig. 8 TGA thermograms of (a) ECL-LPMS and (b) ECL-LPMS-TMS under nitrogen flow at 100 mL min<sup>-1</sup>.

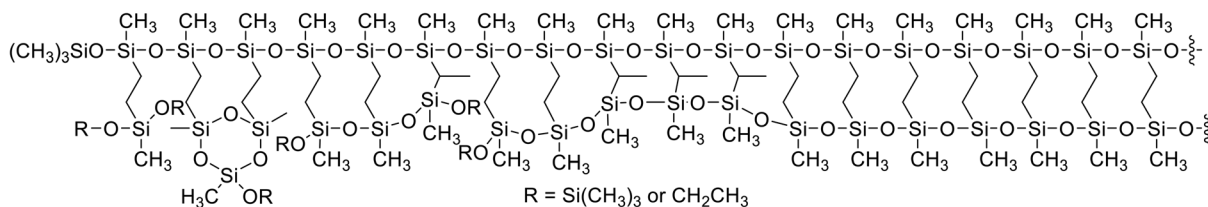


Fig. 7 Proposed molecular structures of ECL-LPMS (R = H or  $\text{CH}_2\text{CH}_3$ ) and ECL-LPMS-TMS (R =  $\text{Si}(\text{CH}_3)_3$  or  $\text{CH}_2\text{CH}_3$ ).

formed under nitrogen flow in the temperature range of  $-150$  °C to  $250$  °C. For PMVS-TMS, a baseline shift attributed to the glass transition temperature ( $T_g$ ) and an endothermic peak corresponding to the melting temperature ( $T_m$ ) were observed at  $-79$  °C and  $-28$  °C, respectively (Fig. 9a). Conversely, no baseline shift or endothermic peak was detected for ECL-LPMS-TMS (Fig. 9b). The  $T_g$  and  $T_m$  values of ECL-LPMS-TMS were estimated to exceed  $200$  °C. These results suggest that the double-chain structure of polysiloxane suppresses the thermal motion of the main chain compared to single-chain polysiloxane, enhancing thermal stability.

### Transparency evaluation of ECL-LPMS and ECL-LPMS-TMS cast films

The transparency of ECL-LPMS and ECL-LPMS-TMS cast films was assessed through UV-Vis measurements. For comparison, aromatic polyimide and Sylgard 184, both heat-resistant polymers, were included in the evaluation. Cast films of ECL-LPMS and ECL-LPMS-TMS were prepared by drop-casting their DIBK solutions onto quartz glass substrates, followed by heating on a hot plate at  $50$  °C for solvent removal. The aromatic polyimide cast film was prepared by coating polyamic acid (Pyre-M. L.® RC-5069, purchased from Sigma-Aldrich) onto glass and heating it at  $300$  °C. Similarly, the Sylgard 184 cast film was prepared by curing the base resin with the curing agent of Dow Sylgard 184. Film thickness, a critical parameter, was *ca.*  $3$ – $4$   $\mu\text{m}$  for ECL-LPMS and ECL-LPMS-TMS, *ca.*  $10$   $\mu\text{m}$  for aromatic polyimide and *ca.*  $5$ – $7$   $\mu\text{m}$  for Sylgard 184. These thickness measurements were performed using a dial gauge. The aromatic polyimide cast film absorbed light at wavelengths below  $500$  nm, causing noticeable coloration (Fig. S3a†). In contrast, ECL-LPMS and ECL-LPMS-TMS cast films exhibited transmittance exceeding  $90\%$  across the wavelength range of  $250$ – $800$  nm (Fig. 10a and b). This level of transparency is comparable to that of the Sylgard 184 cast film (Fig. S3b†). These results demonstrate that ECL-LPMS and ECL-LPMS-TMS are not only thermally stable and soluble but also exhibit excellent transparency.

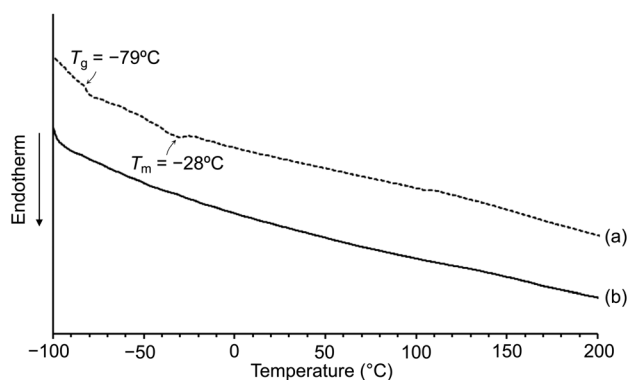


Fig. 9 DSC curves of (a) PMVS-TMS and (b) ECL-LPMS-TMS under nitrogen flow at  $100$  mL  $\text{min}^{-1}$  (third heat-up scan).

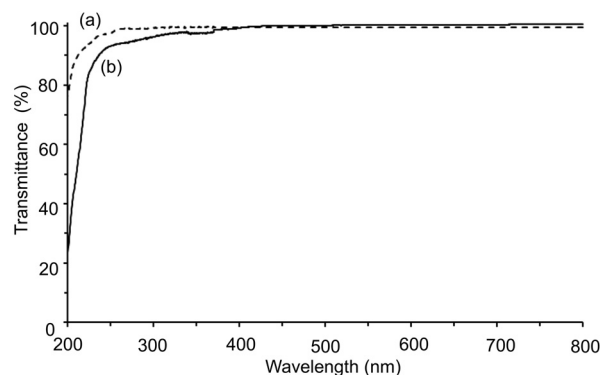


Fig. 10 Transmittance of cast films of (a) ECL-LPMS and (b) ECL-LPMS-TMS.

## Conclusions

In this study, ethylene-crosslinked ladder-like polymethylsiloxanes, ECL-LPMS and ECL-LPMS-TMS, were prepared *via* intramolecular polycondensation (template polymerisation) of PS-DEMS. PS-DEMS, a polysiloxane with diethoxymethylsilyl groups in its side chains, was obtained through hydrosilylation between DEMS and PMVS. Solubility tests, GPC analysis,  $^1\text{H}$  NMR spectroscopy,  $^{29}\text{Si}$  NMR spectroscopy, TEM and WAXD analyses confirmed that ECL-LPMS-TMS has a ladder-like structure comprising two polymethylsiloxane chains interconnected by ethylene linkages. Both ECL-LPMS and ECL-LPMS-TMS exhibited  $T_{d10}$  values exceeding  $500$  °C, with residual weights of  $81\%$  and  $65\%$ , respectively, at  $800$  °C. These results indicate significantly higher thermal stability of these compounds compared to various methyl-containing siloxane compounds. Additionally, ECL-LPMS and ECL-LPMS-TMS cast films exhibited over  $90\%$  transmittance across the UV-Vis range ( $250$ – $800$  nm), indicating high transparency and a colourless appearance. Building on these findings, future efforts will focus on molecular designs enabling the formation of free-standing films in addition to cast films. Furthermore, the potential applications of these materials in optoelectronics and other practical industrial uses are highly promising.

## Author contributions

Conceptualization, Y.K.; data curation, S.N.; formal analysis, S.N.; investigation, S.N.; methodology, S.N.; supervision, Y.K.; writing – original draft, S.N.; writing – review & editing, Y.K.; TEM measurement, K.S.; WAXD measurement, T.H.; discussion on the analysis of molecular and higher-order structures, K.S. and T.H. All authors have read and agreed to the published version of the manuscript.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

## References

- J. K. Pandey, K. R. Reddy, A. P. Kumar and R. P. Singh, *Polym. Degrad. Stab.*, 2005, **88**, 234–250.
- B. Singh and N. Sharma, *Polym. Degrad. Stab.*, 2008, **93**, 561–584.
- M. Hasegawa and K. Horie, *Prog. Polym. Sci.*, 2001, **26**, 259–335.
- L. Vierke, C. Staude, A. Biegel-Engler, W. Drost and C. Schulte, *Environ. Sci. Eur.*, 2012, **24**, 1–12.
- M. Unno, S. Chang and H. Matsumoto, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 1105–1109.
- H. Seki, T. Kajiwara, Y. Abe and T. Gunji, *J. Organomet. Chem.*, 2010, **695**, 1363–1369.
- H. S. Lee, S.-S. Choi, K.-Y. Baek, S. M. Hong, E. C. Lee, J.-C. Lee and S. S. Hwang, *Eur. Polym. J.*, 2012, **48**, 1073–1081.
- Y. Kaneko, N. Iyi, K. Kurashima, T. Matsumoto, T. Fujita and K. Kitamura, *Chem. Mater.*, 2004, **16**, 3417–3423.
- Y. Kaneko, N. Iyi, T. Matsumoto and K. Kitamura, *Polymer*, 2005, **46**, 1828–1833.
- Y. Kaneko, *Polymer*, 2018, **144**, 205–224.
- H. Toyodome, Y. Kaneko, K. Shikinaka and N. Iyi, *Polymer*, 2012, **53**, 6021–6026.
- Y. Kaneko, H. Toyodome, T. Mizumo, K. Shikinaka and N. Iyi, *Chem. – Eur. J.*, 2014, **20**, 9394–9399.
- A. Harada, K. Shikinaka, J. Ohshita and Y. Kaneko, *Polymer*, 2017, **121**, 228–233.
- S. Miyauchi, T. Sugioka, Y. Sumida and Y. Kaneko, *Polymer*, 2015, **66**, 122–126.
- Y. Kaneko, H. Imamura, T. Sugioka and Y. Sumida, *Polymer*, 2016, **92**, 250–255.
- S. Kinoshita, S. Watase, K. Matsukawa and Y. Kaneko, *J. Am. Chem. Soc.*, 2015, **137**, 5061–5065.
- M. Nobayashi, K. Shikinaka and Y. Kaneko, *Polym. J.*, 2022, **54**, 11–20.
- J. F. Brown, Jr., L. H. Vogt Jr., A. Katchman, J. W. Eustance, K. M. Kiser and K. W. Krantz, *J. Am. Chem. Soc.*, 1960, **82**, 6194–6195.
- J. F. Brown, Jr., L. H. Vogt Jr. and P. I. Prescott, *J. Am. Chem. Soc.*, 1964, **86**, 1120–1125.
- Y. Abe and T. Gunji, *Prog. Polym. Sci.*, 2004, **29**, 149–182.
- X. Zhang, P. Xie, Z. Shen, J. Jiang, C. Zhu, H. Li, T. Zhang, C. C. Han, L. Wan, S. Yan and R. Zhang, *Angew. Chem., Int. Ed.*, 2006, **45**, 3112–3116.
- S.-S. Choi, H. S. Lee, S. S. Hwang, D. H. Choi and K.-Y. Baek, *J. Mater. Chem.*, 2010, **20**, 9852–9854.
- Z. Ren, D. Sun, H. Li, Q. Fu, D. Ma, J. Zhang and S. Yan, *Chem. – Eur. J.*, 2012, **18**, 4115–4123.
- H. Kämmerer and S. Ozaki, *Makromol. Chem.*, 1966, **91**, 1–9.
- H. Kämmerer and A. Jung, *Makromol. Chem.*, 1966, **101**, 284–295.
- R. Jantas and S. Polowinski, *J. Polym. Sci., Part A: Polym. Chem.*, 1986, **24**, 1819–1827.
- R. Jantas, *J. Polym. Sci., Part A: Polym. Chem.*, 1990, **28**, 1973–1982.
- R. Jantas, G. Janowska, H. Szocik and S. Polowinski, *J. Therm. Anal. Calorim.*, 2000, **60**, 371–376.
- R. Jantas, J. Szumilewicz, G. Strobin and S. Polowinski, *J. Polym. Sci., Part A: Polym. Chem.*, 1994, **32**, 295–300.
- R. Jantas, S. Polowinski and G. Strobin, *Polym. Int.*, 1995, **37**, 315–318.
- R. Saito, Y. Iijima and K. Yokoi, *Macromolecules*, 2006, **39**, 6838–6844.
- R. Saito and Y. Iijima, *Polym. Adv. Technol.*, 2009, **20**, 280–284.
- S. Matsuo, S. Nonaka, A. Mihata, K. Shikinaka and Y. Kaneko, *Polym. Chem.*, 2025, **16**, 850–857.
- K. Fuchise, M. Igarashi, K. Sato and S. Shimada, *Chem. Sci.*, 2018, **9**, 2879–2891.
- Y. Sugahara, S. Okada, K. Kuroda and C. Kato, *J. Non-Cryst. Solids*, 1992, **139**, 25–34.
- S. Fujikawa, M. Ariyoshi, R. Selyanchyn and T. Kunitake, *Chem. Lett.*, 2019, **48**, 1351–1354.
- L. H. Vogt, Jr. and J. F. Brown Jr., *Inorg. Chem.*, 1963, **2**, 189–192.
- M. G. Voronkov and V. I. Lavrent'yev, *Top. Curr. Chem.*, 1982, **102**, 199–236.
- D. J. Bannister and J. A. Semlyen, *Polymer*, 1981, **22**, 377–381.