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## COMMUNICATION

## Changing the structural and physical properties of 3-arm star poly( $\delta$ -valerolactone)s by a branch-point design

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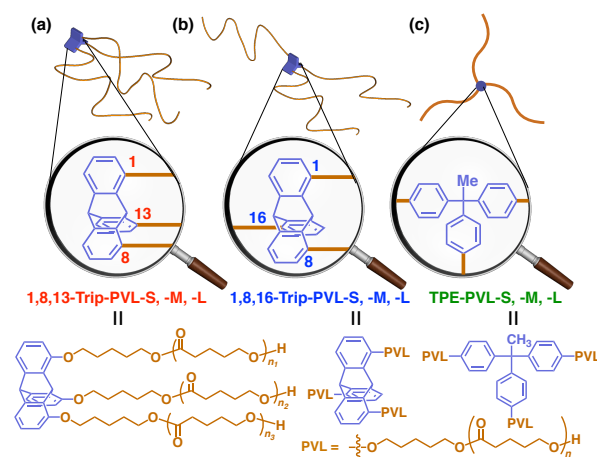
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The chemical structure of a branch point of star-shaped polymers has been considered to have small influence on the physical properties of the entire polymers. Contrary to this general notion, here we show that a 3-arm star polymer, composed of three poly( $\delta$ -valerolactone) arms extended from the one side of a triptycene branch point, exhibits remarkably high complex viscosity, compared to analogous star-shaped polymers with a branch point of a triptycene isomer or a triphenylethane.

The physical properties of polymers are determined not only by the chemical structure of the main and side chains but also by the topology (*i.e.*, shape) of the polymer.<sup>1–3</sup> For instance, Hadjichristidis and coworkers<sup>2</sup> have revealed that star-shaped polymers (Fig. 1) show lower viscosity, smaller hydrodynamic and gyration radii, compared with the corresponding linear-shaped polymers.<sup>1</sup> Although there have been many studies on chain-end effects of polymers,<sup>4</sup> to the best of our knowledge, there is no report on the systematic investigation on chemical structure-dependence of the branch point of star-shaped polymers on their properties.<sup>1</sup> Here we show that the design of branch point could change the properties of star-shaped polymers, would lead to not only updating the general structural perspective of branched polymers but also a conceptually new strategy for tuning physical properties of polymers by the design of branch points.

We have recently reported that 1,8,13-trisubstituted triptycenes and 1,8-disubstituted triptycenes, such as 1,8,13-trialkoxy and 1,8-dialkoxy triptycene, can self-assemble into a "2D+1D" structure at large length scales, where the two-dimensional (2D) sheets formed by nested hexagonal packing of the triptycene units stack into a 1D multilayer structure.<sup>5</sup> This peculiar self-assembling ability is remarkable and enables the formation of 2D+1D structures even when the triptycene functionality is attached to the termini of a liquid polymer, polydimethylsiloxane with  $M_n = 18$ –24 kDa.<sup>5e</sup> These findings prompted us to further test the structuring capability through the construction of a star-shaped polymer using a 1,8,13-trisubstituted triptycene for a branch point that can be regarded as the smallest constituent in polymer.

To investigate how the chemical structure of the branch point of star-shaped polymers affects their properties, we designed the three types of three-arm star-shaped polymers with a different branch point as shown in Fig. 1. The branch point of 1,8,13-Trip-PVLs (Fig. 1a), 1,8,16-Trip-PVLs (Fig. 1b) or TPE-PVLs (Fig. 1c) is composed of 1,8,13-trisubstituted triptycene, 1,8,16-trisubstituted triptycene or 1,1,1-triphenylethane, respectively. We chose poly( $\delta$ -valerolactone) (PVL) as the arms



**Fig. 1.** Schematic illustrations and the chemical structures of three-arm star-shaped polymers (a; 1,8,13-Trip-PVLs, b; 1,8,16-Trip-PVLs and c; TPE-PVLs), in which the branch-point structures are highlighted.

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of the star-shaped polymers, which can readily be grown by living ring-opening polymerization of  $\delta$ -valerolactone from the corresponding hydroxyl group-terminated initiators using diphenyl phosphate as a catalyst.<sup>6</sup> Another merit of this arm design is that PVL has a cross-sectional area similar to those of alkanes and would not impair the self-assembly ability of 1,8,13-trisubstituted triptycene.

To evaluate the effect of molecular weight, we synthesized star-shaped PVLs (Table 1) with different molecular weights by changing the feed ratio of  $\delta$ -valerolactone and initiator (Table S1, ESI<sup>†</sup>). These polymers were obtained with a relatively small molecular weight distribution ( $M_w/M_n$ ) ranging from 1.04 to 1.20. Hereafter, based on the molecular weights, we distinguish the star-shaped PVLs with *ca.* 5.5 kDa, 20 kDa and 41 kDa by adding indexes S (small), M (medium) and L (large), respectively, to the abbreviated name of each polymer. The chemical structures of a total of nine polymers thus obtained were unambiguously characterized by NMR and IR spectroscopy, MALDI-TOF-MS spectrometry. The molecular weights of the star-shaped PVLs, determined by SEC analysis, are shown in Table 1.

In differential scanning calorimetry (DSC), all of the star-shaped PVLs showed an endothermic peak due to melting of the PVL arms (Fig. S1, ESI<sup>†</sup>). Table 1 summarizes the melting points ( $T_m$ ) and associated enthalpy changes ( $\Delta H_m$ ). These values depend on the molecular weight, but not on the chemical structure of the branch point. However, when taking a closer look at the melting behaviors of the polymers, we noticed an interesting difference in the melting behavior for the S-series polymers. As shown in Fig. 2 (see also Mov. S1, ESI<sup>†</sup>), when a solid sample of each S-series polymer was heated at 55 °C (*i.e.*, near the  $T_m$  of the PVL arms), TPE-PVL-S and 1,8,16-Trip-PVL-S underwent melting entirely and partially, respectively (Fig. 2b). Upon subsequent heating at 80 °C, 1,8,16-Trip-PVL-S became liquid entirely (Fig. 2c). In sharp contrast, a sample of 1,8,13-Trip-PVL-S maintained the original shape even after heated up to 80 °C, much higher temperature than the  $T_m$  of the PVL arms, and eventually became liquid at 90 °C (Fig. 2d). Although clear branch-point-structure dependence on the melting behaviors of the M- and L-series polymers was not observed, we thought from the observed behaviors of the S-series polymers that the branch point could have a non-negligible influence on the properties of the polymer.

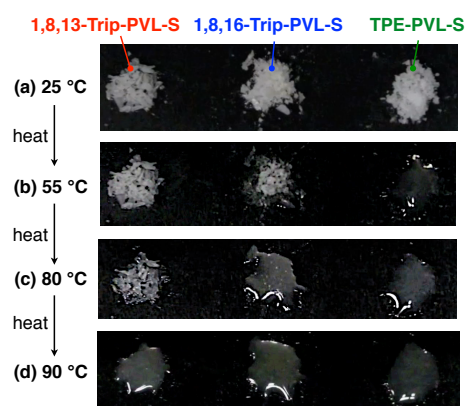
**Table 1.** Structure and properties of 1,8,13-Trip-PVLs, 1,8,16-Trip-PVLs and TPE-PVLs.

PVLs	$M_n^a$ (kDa)	$M_w/M_n^b$	$T_m$ (°C)	$\Delta H_m$ (J/g)	XRD <sup>c</sup>	$\eta^*$ (Pa·s) <sup>d</sup>
1,8,13-Trip-PVL-S	5.5	1.17	47	51	PVL+Trip.	$1.22 \times 10^4$
1,8,16-Trip-PVL-S	5.4	1.20	45	55	PVL+Trip.	$2.35 \times 10^2$
TPE-PVL-S	5.6	1.20	45	50	PVL	$9.88 \times 10^0$
1,8,13-Trip-PVL-M	20.9	1.18	54	70	PVL	$2.13 \times 10^2$
1,8,16-Trip-PVL-M	20.0	1.18	53	70	PVL	$3.18 \times 10^1$
TPE-PVL-M	23.5	1.06	54	78	PVL	$2.63 \times 10^1$
1,8,13-Trip-PVL-L	41.8	1.06	56	72	PVL	$2.65 \times 10^2$
1,8,16-Trip-PVL-L	42.3	1.04	55	70	PVL	$1.95 \times 10^2$
TPE-PVL-L	40.7	1.10	56	67	PVL	$2.66 \times 10^2$

<sup>a</sup>Determined by <sup>1</sup>H NMR measurements. <sup>b</sup>Determined by SEC measurements. <sup>c</sup>The absence or presence of the diffraction from crystallized PVL and assembled triptycene (Trip.) in the XRD profiles measured at 30 °C. <sup>d</sup>Measured at 60 °C, 0.01 Hz.

Variable-temperature X-ray diffraction (VT-XRD) analysis provided insight into the structural change of the star-shaped polymers upon heating. At 30 °C, all the polymers showed diffractions at around  $q = 15, 17$  and  $21 \text{ nm}^{-1}$ , which are characteristic of diffractions from the (110), (200) and (210) planes of crystallized PVL (marked with orange triangles in Fig. 3a–c, g–i, m–o).<sup>7,8</sup> Notably, the XRD profile of 1,8,13-Trip-PVL-S (Fig. 3a) displayed clear diffraction peaks at  $q = 2.86, 5.76, 9.10$  and  $17.9 \text{ nm}^{-1}$  (marked with light blue triangles), along with the diffractions from crystallized PVL. This indicates the presence of a periodic structure other than crystallized PVL. For all the star-shaped polymers, when heated at a temperature (*e.g.*, 60 °C) higher than the  $T_m$  of the PVL arms, the diffraction peaks due to crystallized PVL disappeared (Fig. 3d–f, j–l, p–r). Surprisingly, 1,8,13-Trip-PVL-S, even after melting of the PVL arms, still showed the diffraction peaks at a wide-angle region (light blue triangles in Fig. 3d). Furthermore, a diffraction peak at  $q = 15.3 \text{ nm}^{-1}$ , which had been hidden by diffractions from crystallized PVL, was newly detected. The XRD pattern of 1,8,13-Trip-PVL-S at 60 °C is very similar to those typically observed for 1,8,13-trisubstituted triptycene assemblies.<sup>2a</sup> Indeed, all the diffraction peaks at 60 °C were successfully indexed by assuming a "2D+1D" structure with  $d$ -spacing of  $d_{001} = 2.15, d_{002} = 1.08, d_{100} = 0.69, d_{110} = 0.40, d_{111} = 0.39, d_{200} = 0.35$  and  $d_{201} = 0.34 \text{ nm}$ , where the triptycene branch points assemble to form 2D hexagonal layers ( $a = 0.80 \text{ nm}$ ), which are aligned one-dimensionally ( $c$ -axis) with a 2.16 nm separation (Table S2, ESI<sup>†</sup>).

Fig. 4a illustrates a presumable assembly structure of 1,8,13-Trip-PVL-S featuring molecular ordering of the triptycene moiety. Although it is difficult to address how the PVL arms are located in the polymer assembly structure, the polymer chains might be extended out of the 2D triptycene assembly through a gap between triptycene units (Fig. 4a, right). Fig. 4b shows the detailed VT-XRD patterns of 1,8,13-Trip-PVL-S measured at 30–150 °C. The diffraction peaks originating from the 2D+1D structure gradually decreased with increasing temperature and almost disappeared at 130 °C. This indicates that the triptycene assembly can be maintained even in the molten state of the PVL arms (Fig. 4c). Such strong structuring ability of the triptycene branch point in 1,8,13-Trip-PVL-S is considered responsible for



**Fig. 2.** Changes in the appearance of a solid sample of 1,8,13-Trip-PVL-S, 1,8,13-Trip-PVL-S or TPE-PVL-S upon heating on a hot plate (a; 25 °C, b; 55 °C, c; 80 °C and d; 90 °C). See also Mov. S1, ESI<sup>†</sup>.

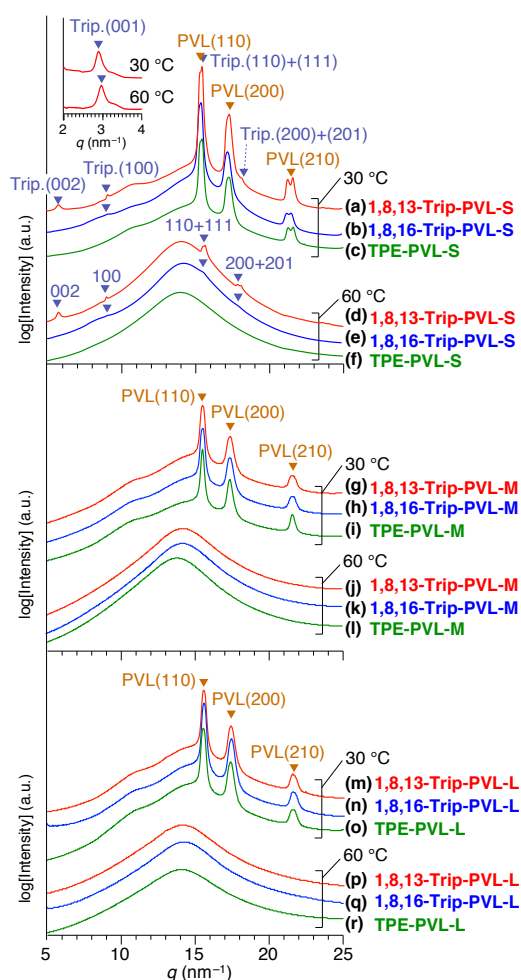
the shape-retaining property upon heating over  $T_m$  of the PVL arms (Fig. 2).

Meanwhile, diffractions due to a 2D+1D structure of the triptycene branch points were absent in the XRD profiles of the M-series (Fig. 3g–l) and L-series polymers (Fig. 3m–r), as well as TPE-PVL-S (Fig. 3c,f). However, on close inspection of the XRD profiles of 1,8,16-Trip-PVL-S at 30 and 60 °C (Fig. 3b,e, see also Fig. S2, ESI<sup>†</sup>), very weak peaks were detected at  $q = 9.10$ , 15.3 and 17.9 nm<sup>-1</sup> (marked with light blue triangles), which can be attributed to diffractions from the (100), (110) and (200) planes of a 2D assembly of the triptycene branch point. The weak assembly feature of the triptycene branch point in 1,8,16-Trip-PVL-S is consistent with the partial melting behavior of this polymer (Fig. 2).

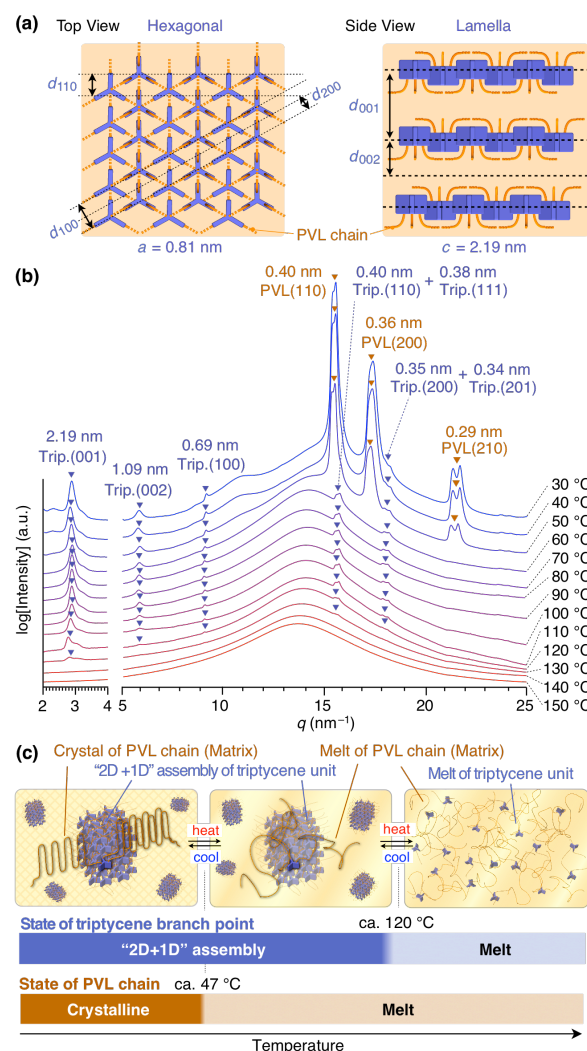
Rheological measurements allowed quantitative analysis of the mechanical properties of the star-shaped PVLs (Fig. 5, Figs. S3–S5, ESI<sup>†</sup>). Fig. 5a–c show the frequency dependence of complex viscosity ( $\eta^*$ ) of the polymers measured using a rotational rheometer at 60 °C.<sup>9–11</sup> Over frequency range from 0.01 to 10 Hz, TPE-PVLs (Fig. 5a–c, green) have almost constant  $\eta^*$  values of 10<sup>0</sup>, 10<sup>1</sup> and 10<sup>2</sup> Pa·s for TPE-PVL-S, TPE-PVL-M and

TPE-PVL-L, respectively (Table 1), representing typical behavior of Newtonian fluid.<sup>10</sup> Notably, the  $\eta^*$  value of 1,8,13-Trip-PVL-S at 10 Hz is *ca.* 10<sup>2</sup> Pa·s, it gradually increases with decreasing frequency and reaches to *ca.* 10<sup>4</sup> Pa·s at 0.01 Hz. This pseudoplastic behavior<sup>10</sup> may originate from the increase in apparent molecular weight, caused by the assembly of the triptycene branch point that results in the 2D+1D periodic order of 1,8,13-Trip-PVL-S.<sup>3</sup> Likewise, 1,8,16-Trip-PVL-S was found to behave as a pseudoplastic material and its  $\eta^*$  values increase from *ca.* 10<sup>0</sup> to 2×10<sup>2</sup> Pa·s with decreasing frequency from 10 to 0.01 Hz (Fig. 5a, blue). The fact that 1,8,16-Trip-PVL-S has much smaller  $\eta^*$  than 1,8,13-Trip-PVL-S in the entire measurement frequency range is consistent with the difference in the melting and structuring behaviors between these polymers (Figs. 2 and 3).

Interestingly, among the M-series polymers, only 1,8,13-Trip-PVL-M showed pseudoplastic behavior to provide enhanced  $\eta^*$  in the low frequency range (Fig. 5b, red), although this polymer does not exhibit XRD diffractions associated with a



**Fig. 3.** XRD patterns of the S-series (a–f), M-series (g–l) and L-series (m–r) polymers of 1,8,13-Trip-PVLs (red), 1,8,16-Trip-PVLs (blue) and TPE-PVLs (green) measured at 30 °C (a–c, g–i, m–o) and 60 °C (d–f, j–l, p–r) in a glass capillary with a diameter of 1.5 mm. Inset in (a) represents small-angle diffraction profiles of 1,8,13-Trip-PVL-S at 30 and 60 °C.

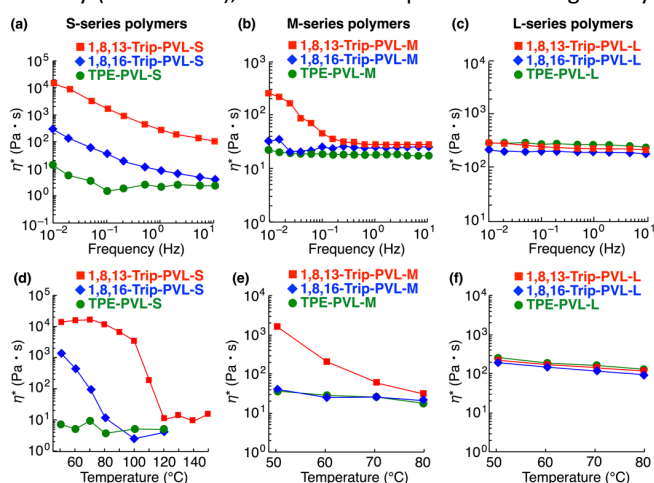


**Fig. 4.** (a) Schematic illustration of the assembly structure of 1,8,13-Trip-PVL-S at 25 °C. (b) VT-XRD profiles of 1,8,13-Trip-PVL-S measured upon heating in a glass capillary with a diameter of 1.5 mm. (c) Schematic diagram showing the relationship between the two periodic structures formed in the bulk phase of 1,8,13-Trip-PVL-S and their thermal stability.

periodic 2D+1D structural order (Fig. 3g,j). We presume that the triptycene branch point of 1,8,13-Trip-PVL-M may assemble to form a 2D+1D structure at least partially, but the content of the triptycene branch point (~1.2 wt%) in 1,8,13-Trip-PVL-M ( $M_n = 20$  kDa) was too small to be detected by XRD and DSC experiments. Noteworthy is the fact that even such a small content, the triptycene branch point has significant impact on the mechanical properties of the star-shaped polymer. Considering also the fact that the L-series polymers all behave as Newtonian fluid (Fig. 5c), when the triptycene content relative to the PLV arms is further reduced, the effect would no longer be manifested.

As shown in Fig. 5d–f, the trends in the temperature dependence of  $\eta^*$  is similar to those in the frequency dependence (Fig. 5a–c). There is no apparent difference among the L-series polymers (Fig. 5f). The  $\eta^*$  values of 1,8,13-Trip-PVL-M (Fig. 5e, red) rapidly decrease as the temperature increases and become almost identical to those of 1,8,16-Trip-PVL-M and TPE-PVL-M (Fig. 5e, blue and green) at 80 °C. More notable difference was found in the behaviors of the S-series (Fig. 5d). 1,8,16-Trip-PVL-S (Fig. 5d, blue) also showed a rapid decrease in  $\eta^*$  with increasing temperature, providing a value similar to those of TPE-PVL-S (Fig. 5d, green) over 100 °C. While the  $\eta^*$  values of 1,8,13-Trip-PVL-S (Fig. 5d, red) are scarcely changed up to 100 °C, upon further heating, they rapidly decreased to reach plateau over 120 °C. This feature agrees well with that of the VT-XRD of 1,8,13-Trip-PVL-S (Fig. 4b,c) and clearly indicates a close relationship between  $\eta^*$  and structuring of the triptycene branch point.

In conclusion, we have shown the melting, structural, and rheological behaviors of three-arm star-shaped PVLs in relation to the chemical structure of the branch point. Notably, a 1,8,13-trisubstituted triptycene, when used as the branch point of the small- ( $M_n = 5.5$  kDa) and medium-size ( $M_n = 20$  kDa) polymers with a triptycene content of ~4.5 wt% and ~1.2 wt%, respectively, resulted in the improvement of the complex viscosity (0.01~10 Hz), thanks to its superb assembling ability.<sup>5</sup>



**Fig. 5.** Frequency dependence of  $\eta^*$  of the S-series (a), M-series (b) and L-series (c) polymers of 1,8,13-Trip-PVLs (red), 1,8,13-Trip-PVLs (blue) and TPE-PVLs (green) measured at 60 °C. Temperature dependence of  $\eta^*$  of the S-series (d), M-series (e) and L-series (f) polymers of 1,8,13-Trip-PVLs (red), 1,8,13-Trip-PVLs (blue) and TPE-PVLs (green) measured at a frequency of 0.01 Hz.

To the best of our knowledge, this study demonstrates for the first time that polymer properties can be modulated by the design of branch points. Using other types of multi-arm branched polymers, further investigations to clarify the scope and limitation of the triptycene branch point as a module to change polymer properties are underway in our group.

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## Conflicts of interest

There are no conflicts to declare.

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- All the polymers are in a terminal flow region without chain entanglement in the temperature and frequency regions.
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- The  $\eta^*$  values of TPE-PVL-M and linear PVL with a similar  $M_n$  are comparable to one another (Fig. S6, ESI<sup>†</sup>).