Electronic Supplementary Information (ESI) for

Effect of alkyl side chain length on microscopic structures and mechanical properties of ionically-functionalized block polymer-based thermoplastic elastomers

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GPC chromatograms of neat SIS and s-SIS.

Fig. S1 shows the GPC chromatograms of neat SIS and s-SIS. By calibrating the molecular weights with polystyrene standards, the number average molecular weight (M_n) and the dispersity (M_w/M_n) of neat SIS were determined to be 166k and 1.07, respectively. The peak of chromatogram of s-SIS slightly shifted to a lower elution time than that of neat SIS due to the increase in the apparent molecular weight of the polymer,[1] and the calibrated M_n and M_w/M_n of s-SIS were estimated to be 167k and 1.08, respectively.

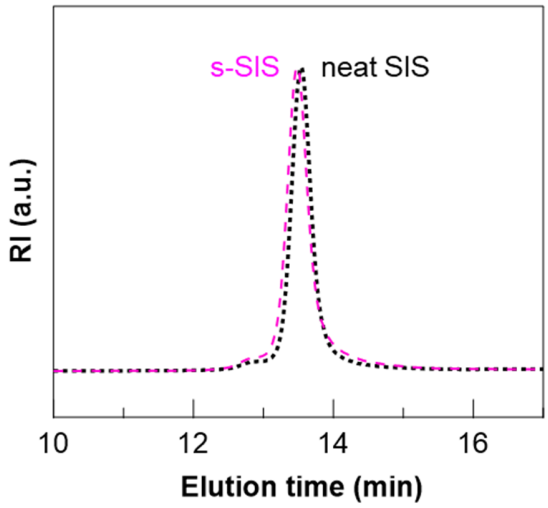

Fig. S1 GPC chromatograms of neat SIS (black dotted line), s-SIS (pink dashed line).

^{1}H NMR spectrum of neat SIS.

Fig. S2 presents the ^{1}H NMR spectrum of neat SIS. The peaks at 6.2 to 7.2 ppm originate from five protons on the phenyl groups of the polystyrene (a, b and c). The peaks originating from one proton on the C=C double bond of the 1,4-polyisoprene (d), and two protons on the C=C double bond of the 3,4-polyisoprene (e) appear at 4.9 to 5.3 ppm, and 4.5 to 4.9 ppm, respectively. The mole fraction of the polystyrene block in neat SIS was estimated to be 0.13. Thus, the weight fraction of the polystyrene block in neat SIS was estimated to be 0.19. This estimation was based on the integral of the peaks of a–e.

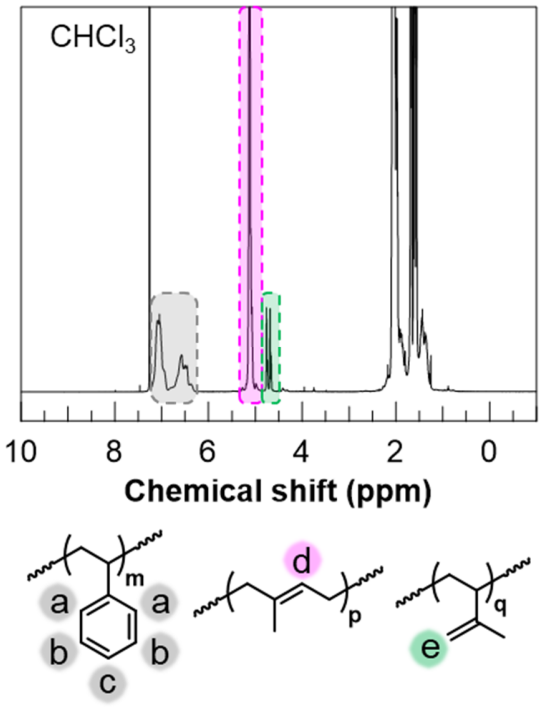

Fig. S2 ^{1}H NMR spectrum of neat SIS.

FT-IR spectra of h-SIS(*n*) and i-SIS(*n*).

Fig. S3 shows the FT-IR spectra of h-SIS(*n*) and i-SIS(*n*) with n = 4, 8, and 12 in the range of 1500–2000 cm^{-1}, and 3100–3600 cm^{-1}. Similar to the spectrum of h-SIS(1), in the spectra of h-SIS(4), h-SIS(8) and h-SIS(12), absorptions appeared around 1710–1730 cm^{-1} and 1640 cm^{-1}, corresponding to the C=O stretching vibrations of the carboxyl group and amide group, respectively. In addition, the spectra of h-SIS(4), h-SIS(8) and h-SIS(12) showed broad absorption bands at approximately 3230–3470 cm^{-1}, corresponding to the O–H stretching vibration of the hydrogen-bonded carboxyl group and the N–H stretching vibration of the hydrogen-bonded amide group.

Similar to the spectrum of i-SIS(1), in the spectra of i-SIS(4), i-SIS(8) and i-SIS(12), the absorption at 1710–1730 cm^{-1} nearly disappeared, while a new absorption band corresponding to the stretching vibration of the ionic carboxylate group appeared around 1570 cm^{-1}. In addition, the absorption range around 3230–3470 cm^{-1} observed in the spectrum of h-SIS(*n*) slightly shifted to approximately 3170–3500 cm^{-1}, indicating the successful conversion of the carboxy group to the carboxylate group.

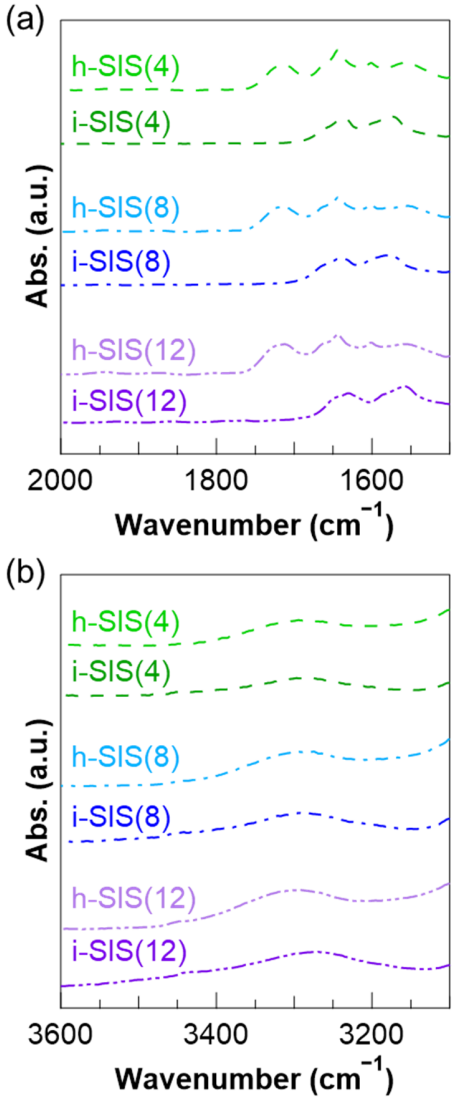

Fig. S3 FT-IR spectra of h-SIS(4) (light green dashed line), i-SIS(4) (green dashed line), h-SIS(8) (light blue dashed-dotted line), i-SIS(8) (blue dashed-dotted line), h-SIS(12) (light purple dashed-two-dotted line), and i-SIS(12) (purple dashed-two-dotted line) within the wavenumber ranges of (a) 1500 to 2000 cm^{-1} and (b) 3100 to 3600 cm^{-1}.

Reference

1. T. Kajita, H. Tanaka, A. Noro, Y. Matsushita, A. Nozawa, K. Isobe, R. Oda and S. Hashimoto, *Polymer*, 2021, **217**, 123419.