Electronic Supplementary Material (ESI) for Polymer Chemistry.

- Electronic Supplementary Information -

Additional Crystalline Structure of Syndiotactic Polystyrene Composites with Acetylated Cyclodextrin

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Content

1. Materials

Deuterated chloroform was purchased from Sigma-Aldrich. 1,2,4-Trichlorobenzene and tetramethylsilane (TMS) were obtained from Tokyo Chemical Industry Co., Ltd. Syndiotactic polystyrene copolymerized with *p*-methyl styrene (sPS-MS) was kindly provided from Idemitsu Kosan Co., Ltd. Acetylated α-cyclodextrin (AcαCD), acetylated β-cyclodextrin (AcβCD) and acetylated γ-cyclodextrin (AcγCD) were prepared according to previous report.[1]

2. Measurements

NMR spectroscopy:

The ^{1}H NMR were recorded with a JEOL ECS-500 NMR spectrometer at 23 °C. The chemical shifts are referenced to the signal of TMS (δ = 0 ppm for ^{1}H NMR). 15.6 mg of sPS-MS and 303 mg of AcβCD were dissolved in respective 3 mL of $CDCl_3$ (0.05 M each). Subsequently, two solutions were mixed with different volume ratios to result in 500 μL solutions (0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10, and 100/0). Finally, 1 μL of TMS was added to each mixed solution. For AcαCD and AcγCD mixtures, 130 mg of AcαCD and 173 mg of AcγCD were dissolved in respective 1.5 mL of $CDCl_3$ (0.05 M). Each solution was mixed with the sPS-MS solution to result in 600 μL solutions with various volume ratios (0/100, 30/70, 50/50, 70/30, and 100/0).

Wide angle X-ray scattering (WAXS) measurement:

Internal structures of films were determined by WAXS at BL19B2 beam line in SPring-8, Nishi-harima, Japan. The power of the incident X-ray beams was 18 keV. The sample-to-detector lengths for WAXS was 100 mm. The scattering angle in the WAXS measurements was expressed as 2 theta.

Differential scanning calorimeter (DSC) measurements:

The thermal behaviours of the sPS-MS composites were determined by differential scanning calorimeter (Hitachi High-Technologies Corporation, DSC7020 System). On the first scan, samples were cooled to 0 ºC at the rate of 10 ºC/min and held for 5 minutes heated to 300 °C at the same rate. The second scans were carried out repeating the same processes.

3. Preparation of sPS-MS composite film with acetylated CD (sPS-MS/AcCD)

Table S1. Amount of sPS-MS and AcαCD for film preparation.

sPS-MS weight ratio (wt%)	sPS-MS (mg)	AcαCD (mg)	TCB (mL)
100	491	-	5
99	510	4.8	5
97	497	15	5
95	510	26	5

Table S2. Amount of sPS-MS and AcβCD for film preparation.

sPS-MS weight ratio (wt%)	sPS-MS (mg)	AcβCD (mg)	TCB (mL)
100	491	-	5
99	490	5.4	5
97	501	15.2	5
95	497	26.3	5

Table S3. Amount of sPS-MS and AcγCD for film preparation

sPS-MS weight ratio (wt%)	sPS-MS (mg)	AcγCD (mg)	TCB (mL)
100	491	-	5
99	503	7.3	5
97	487	15.9	5
95	481	24.4	5

4. NMR spectra of mixtures of sPS-MS/AcCD

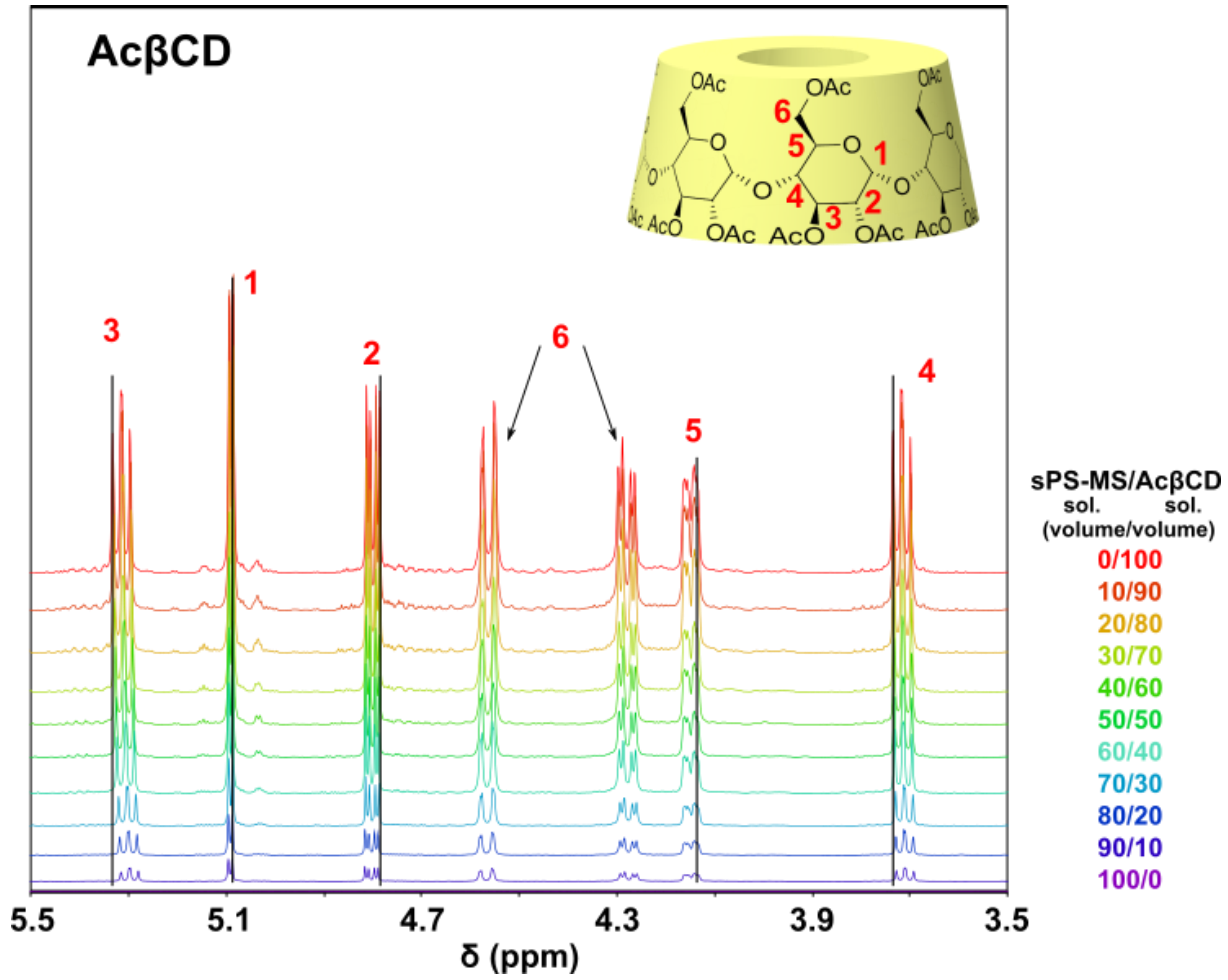

Fig. S1. Zoomed NMR spectra of the sPS-MS/AcβCD for chemical shifts of AcβCD with various mixing ratios (3.5-5.5 ppm).

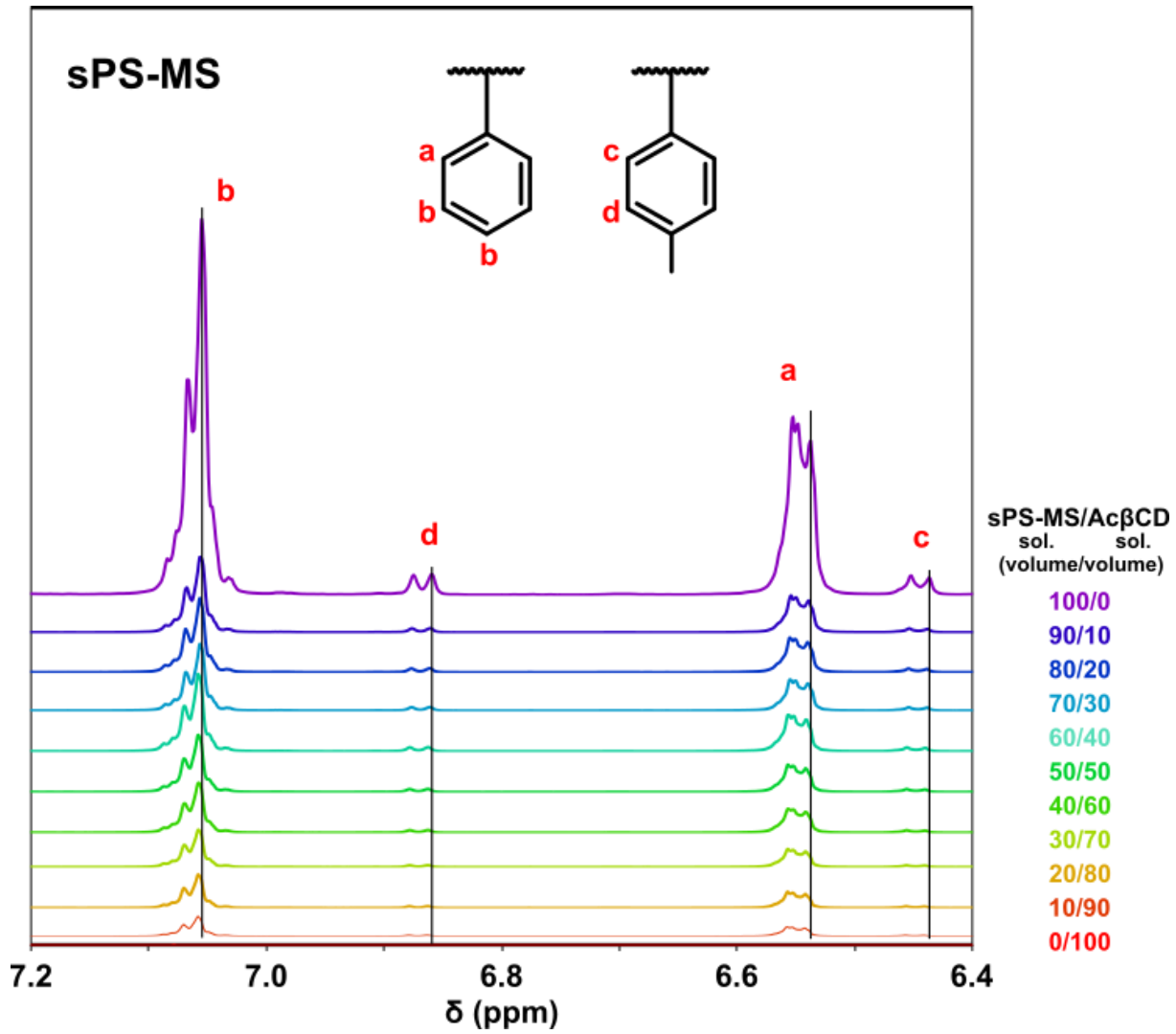

Fig. S2. Zoomed NMR spectra of the sPS-MS/AcβCD for chemical shifts of the benzene rings on sPS-MS with various mixing ratios (6.4-7.2 ppm).

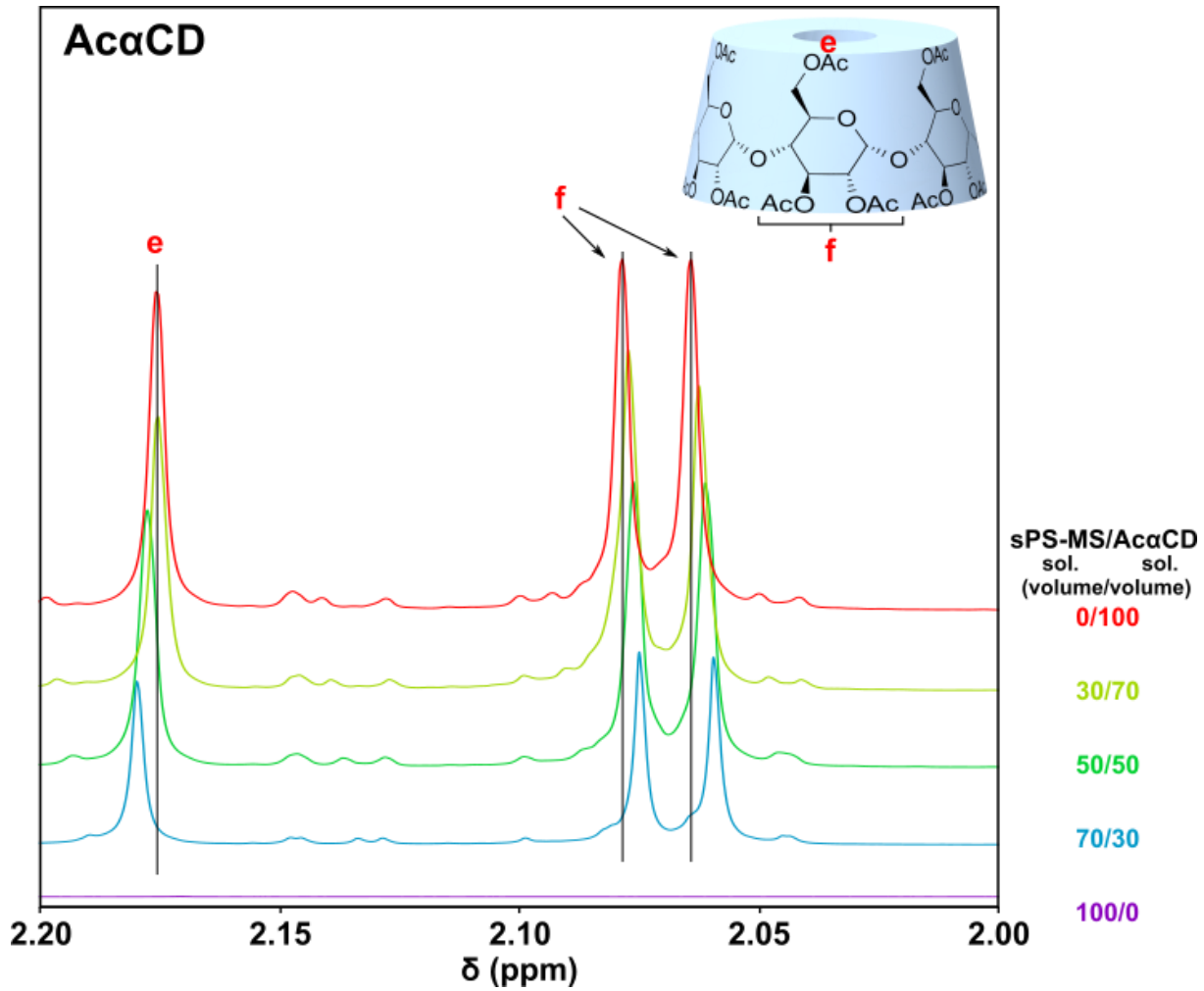

Fig. S3. Zoomed NMR spectra of the sPS-MS/AcαCD for chemical shifts of AcαCD with various mixing ratios (2.0-2.2 ppm). The acetyl groups on primary rim (e) downfield shifted and those on secondary rim (f) upfield shifted because of the deshielding and shielding effects, respectively.

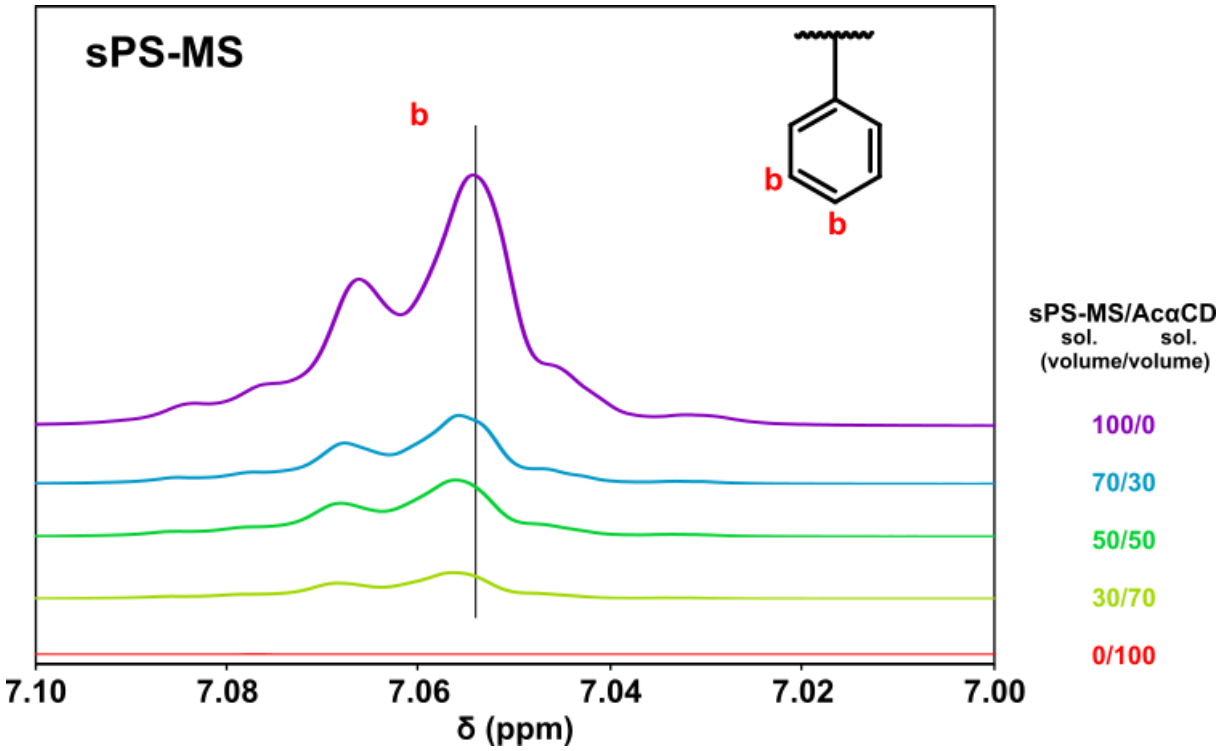

Fig. S4. Zoomed NMR spectra of the sPS-MS/AcαCD for chemical shifts of the benzene rings on sPS-MS with various mixing ratios (7.0-7.1 ppm).

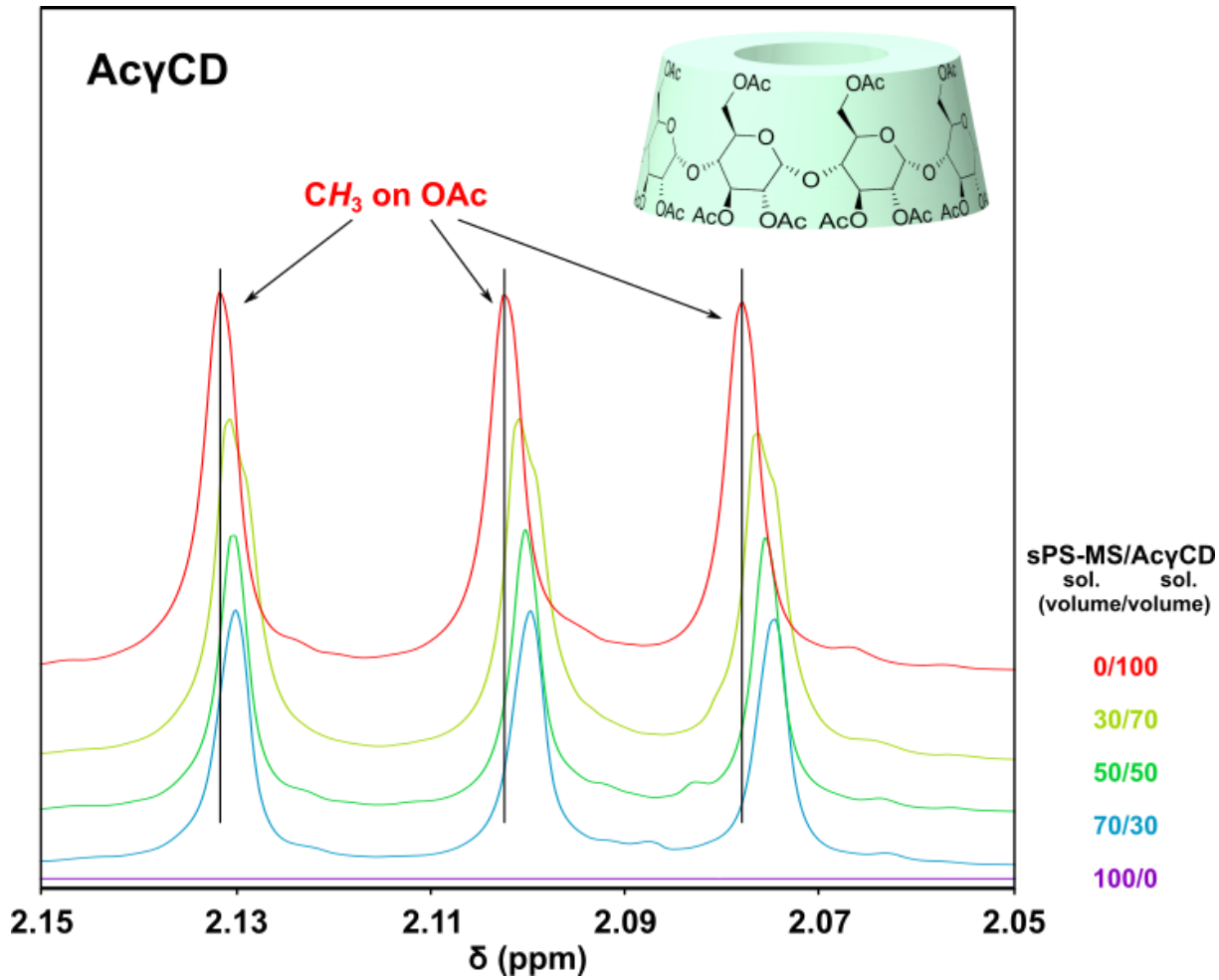

Fig. S5. Zoomed NMR spectra of the sPS-MS/AcγCD for chemical shifts of AcγCD with various mixing ratios (2.05-2.15 ppm). All acetyl groups upfield shifted because of the shielding effect.

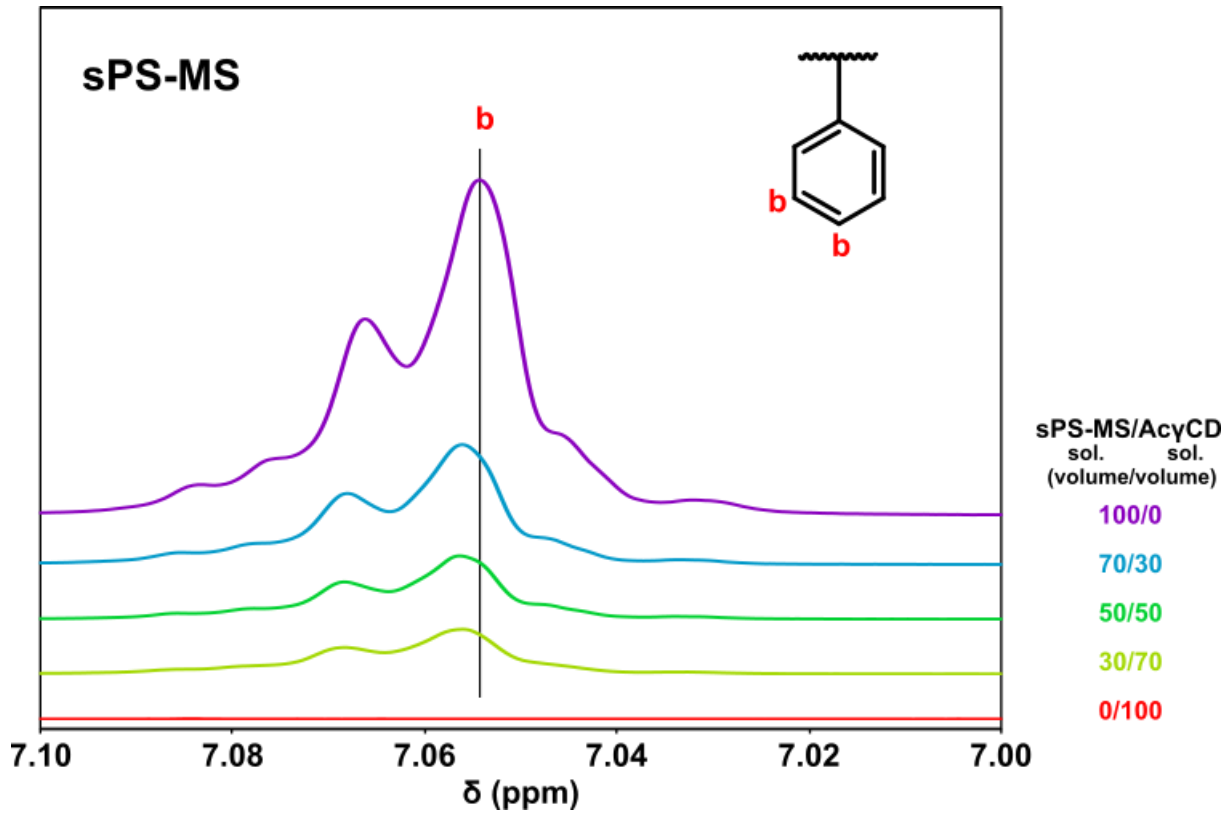

Fig. S6. Zoomed NMR spectra of the sPS-MS/AcγCD for chemical shifts of the benzene rings on sPS-MS with various mixing ratios (7.0-7.1 ppm).

4. Comparison of peak areas of WAXS profiles of sPS-MS/AcCD

For peak area comparison the peaks at 4.6º were chosen as standard, as the peaks were almost constant in the experiments.

Table S4. Amount of sPS-MS and AcαCD for film preparation.

Types of AcCD	Peak area at 2.7º / Peak area at 4.6º		Peak area at 5.4º / Peak area at 4.6º	
	1 wt%	3 wt%	1 wt%	3 wt%
AcαCD	0.21	0.26	0.16	0.20
AcβCD	2.08	0.46	1.79	0.38
AcγCD	1.13	1.60	0.95	1.39

5. Thermal properties of sPS-MS/AcCD at second DSC scan

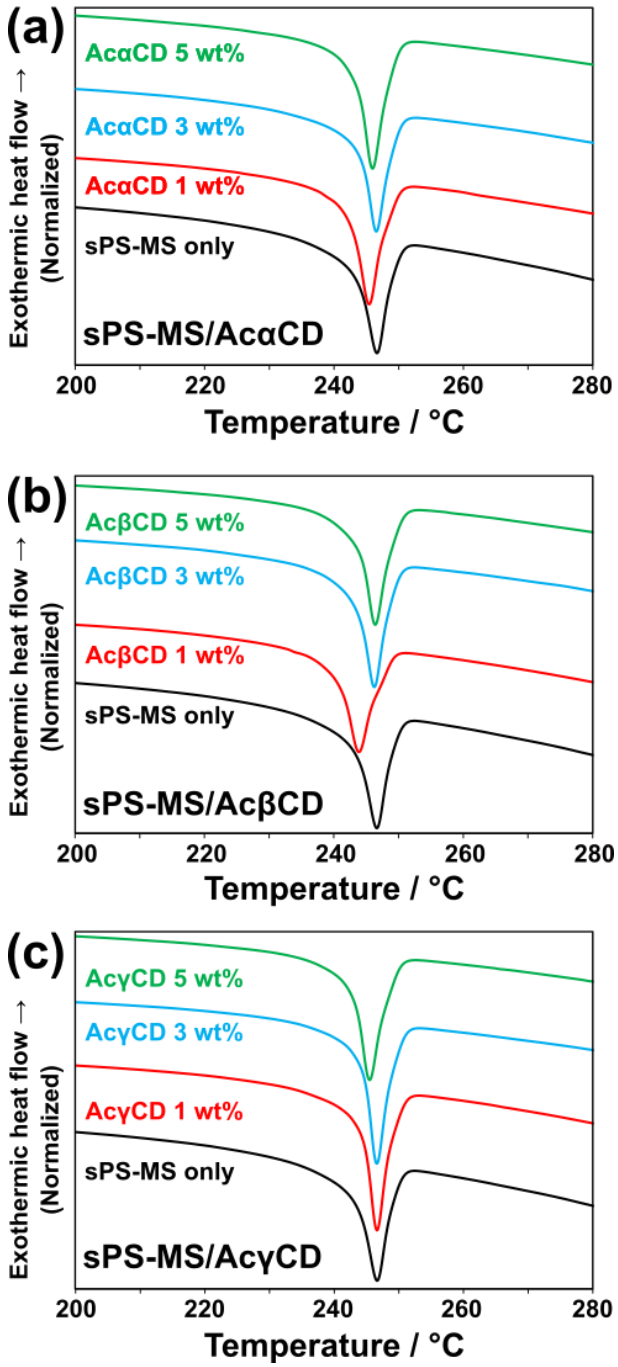

Fig. S7. DSC thermograms of the sPS-MS composites under the second scan with (a) AcαCD, (b)AcβCD, and (c) AcγCD.

References

1 J. Park, S. Murayama, M. Osaki, H. Yamaguchi, A. Harada, G. Matsuba and Y. Takashima, *Eur. Polym. J.*, 2020, **134**, 109807.