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Rheological behavior of thread-like fiber solutions formed from a rosin-based surfactant with two head groups

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1. Synthesis

1.1 Synthesis of R-11-3-DA

The detailed synthetic process, which is shown in **Figure 1**, is described as follows.

(1) synthesis of Methyl 11-aminoundecanoate hydrochloride. 11-aminoundecylic acid (20.1 g, 0.10 mol) and methanol (32.0 g, 1.00 mol) were added into a 500ml three-necked flask. Thionyl chloride (14.3 g, 0.12 mol) was added dropwise at 50 °C. Acidic gas was generated during this process, and it was adsorbed by a saturated NaOH solution. After the addition, the mixture was stirred at 0 °C for 1 hours and at 70 °C for 6 h. After cooling, the reaction mixture was evaporated under reduced pressure to remove the excessive thionyl chloride and methanol. The residue was recrystallized with methanol and ethyl acetate three times. The final product was obtained as a white solid after being dried under vacuum at 50 °C. Yield: 86.5%.

(2) synthesis of Compound **1**. Purified dehydroabietic acid (21 g, 0.07 mol) and a catalytic amount of 4-dimethylaminopyridine (DMAP) were added into a 250ml three-necked flask. Thionyl chloride (10 g, 0.105 mol) was added dropwise at 35 °C. Acidic gas was generated during this process, and it was adsorbed by a saturated NaOH solution. After the addition, the mixture was stirred at 35 °C for 5 hours. After cooling, the excessive thionyl chloride was removed under reduced pressure and

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dehydroabietic chloride was obtained. The obtained dehydroabietic chloride (22.3 g, 0.07 mol) was dissolved into CH_2Cl_2 and added dropwise into a three-necked flask filled with 11-aminoundecanoate hydrochloride (21.1 g, 0.084mol) and trimethylamine (28.0 g, 0.28 mol) at 0 °C. After the addition, the reaction continued for another 3 hours. And then the reaction mixture was washed with deionized water three times and extracted with CH_2Cl_2 one time. The extractions were combined and dried using anhydrous Na_2SO_4 for 2 hours. The mixture was evaporated under reduced pressure to remove the remaining solvent and triethylamine. The residue was purified on a silica gel column (300-400 mesh) using petroleum ethyl acetate / petroleum ether (1:6) as the eluent. Compound **1** was obtained as yellow, viscous liquid after the removal of the solvent. Yield: 87.6%.

(3) synthesis of Compound **2**. A mixture of R-11-Me (30 g, 0.06 mol), 3-dimethylaminopropyl amine (18.5 g, 0.18 mol) and a catalytic amount of KOH was added into a 250 mL single-necked flask and was stirred at 100 °C for 18 hours under condensed reflux. After cooling, the reaction mixture was evaporated under reduced pressure to remove the excessive 3-dimethylaminopropyl amine. The residue was purified on a silica gel column (300-400 mesh) using petroleum ether/ethyl acetate (1:5) as the eluent. The final product was obtained as yellow, viscous liquid after the removal of the solvent and being dried under vacuum at 55 °C. Yield: 75.3%.

(4) synthesis of R-11-3-DA. A mixture of Compound **2** (22.7 g, 0.04 mol), 3-bromo-N,N,N-trimethylpropan-1-aminium Bromide (6.5g，0.036 mol) and 150 ml ethanol was added into a 500 mL single-necked flask and was stirred at 90 °C for 72 hours under condensed reflux. After cooling, the mixture was evaporated under reduced pressure to remove ethanol. The residue was recrystallized with ethanol and acetone one time and was washed with acetone three times. R-11-3-DA was obtained as a white solid after being dried under vacuum at 35 °C. Yield: 65.2%.

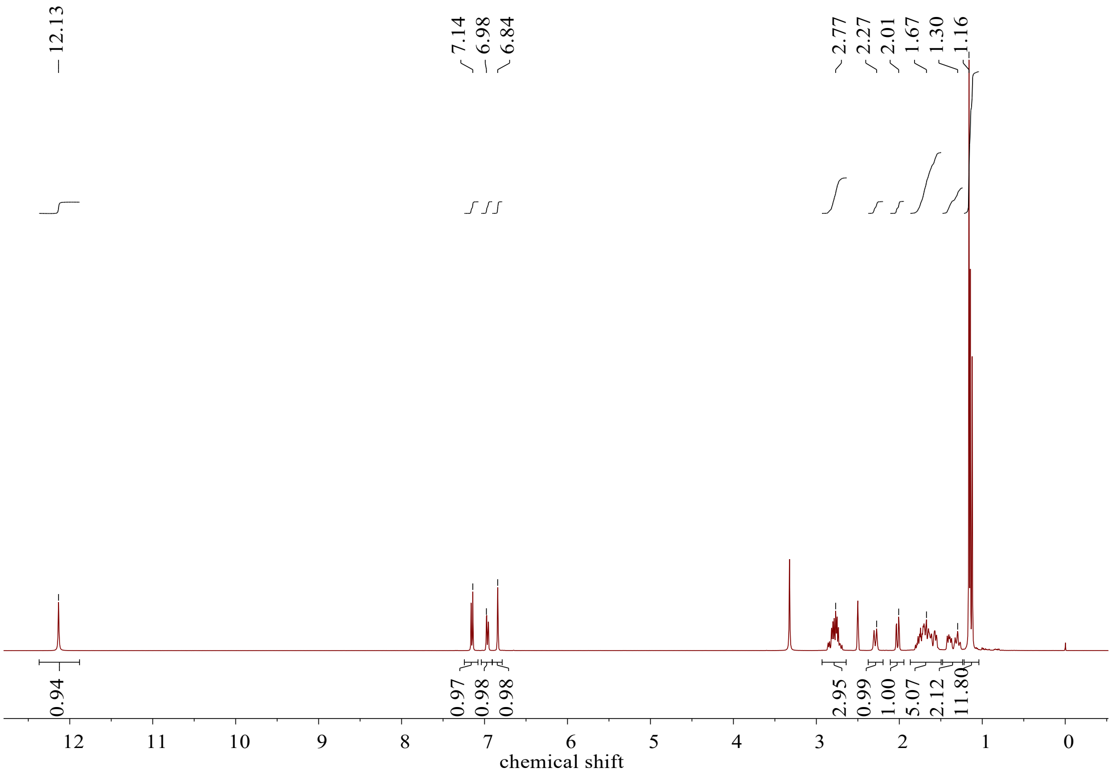
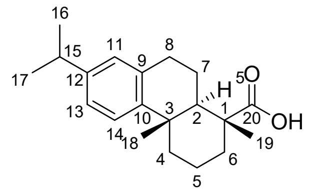


Fig. S1 ^{1}H NMR spectrum of dehydroabietic acid (DMSO)



^{1}H NMR (400 MHz, DMSO) : δ 12.13 (s, 1H, COOH), 7.14 (d, 1H, C14-1H), 6.98 (d, 1H, C13-1H), 6.84 (s, 1H, C11-1H), 2.88-2.68 (m, 3H, C8-2H, C15-1H), 2.27 (d, 1H, C4-1H), 2.03 (d, 1H, C2-1H), 1.82-1.54 (m, 5H, C5-2H, C6-2H, C7-1H), 1.44-1.26 (m, 2H, C4-1H, C7-1H), 1.16 (s, 6H, C16-3H, C17-3H), 1.14 (s, 3H, C19-3H), 1.12 (s, 3H, C18-3H).

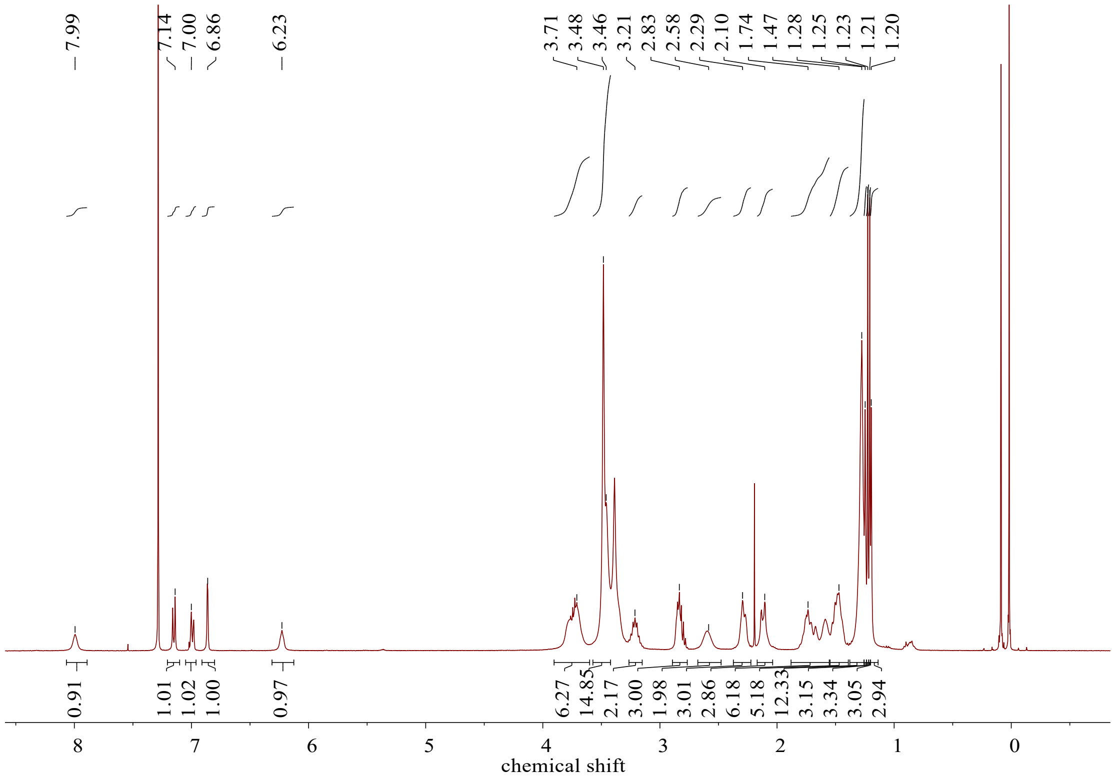
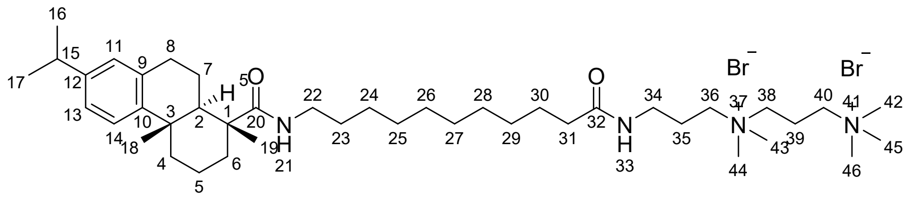


Fig. S2 ^{1}H NMR spectrum of R-11-3-DA (CDCl$_3$)



^{1}H NMR (400 MHz, CDCl$_3$): δ 7.99 (s, 1H, N21-1H), 7.14 (d, 1H, C14-1H), 7.00 (d, 1H, C13-1H), 6.86 (s, 1H, C11-1H), 6.23 (s, 1H, N33-1H), 3.85-3.63 (m, 6H, C36-2H, C38-2H, C40-2H), 3.48 (s, 9H, C42-3H, C45-3H, C46-3H), 3.46 (s, 6H, C43-3H, C44-3H), 3.21 (m, 2H, C22-2H), 2.88-2.77 (m, 3H, C8-2H, C15-1H), 2.58 (s, 2H, C39-2H), 2.29 (m, 3H, C4-1H, C34-2H), 2.10 (m, 3H, C2-1H, C35-2H), 1.84-1.55 (m, 6H, C7-2H, C4-1H, C5-1H, C6-2H), 1.55-1.41 (m, 5H, C5-1H, C23-2H, C30-2H), 1.28 (s, 12H, C24-2H, C25-2H, C26-2H, C27-2H, C28-2H, C29-2H), 1.25 (s, 3H, C19-3H), 1.23 (s, 3H, C16-3H), 1.21 (s, 3H, C20-3H), 1.20 (s, 3H, C17-3H).

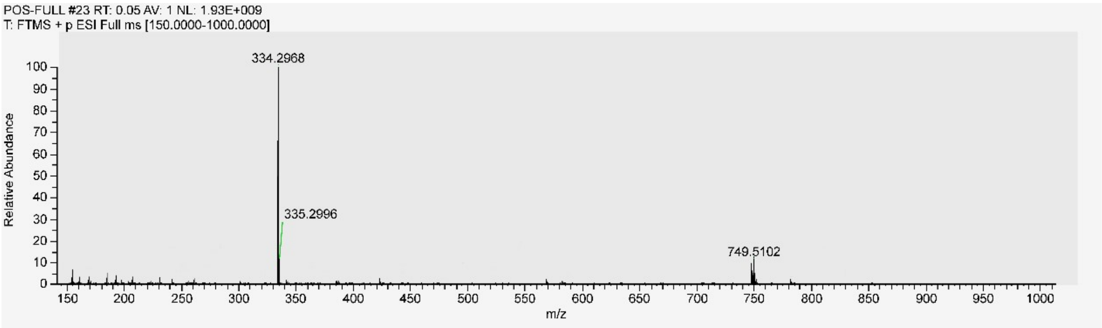


Fig. S3 HRMS of R-11-3-DA

HRMS m/z calcd for $C_{42}H_{76}N_2O_4^{2+}$ (M-2Br): 334.2979, found 334.2968.

1.2 Synthesis of Sodium Laurate

(1) Synthesis of Methyl Laurate. A mixture of lauric acid (100 g, 0.5 mol), methanol (80 g, 2.5 mol) and a catalytic amount of H_2SO_4 in a three-necked flask was added into a 500 mL single-necked flask and was stirred at 70 °C for 6 hours under condensed reflux. After cooling, 100 mL of deionized water was added to separate the layers, and the upper layer was collected and dried with anhydrous magnesium sulfate. The methyl ester was distilled under reduced pressure, and the fraction at 120 °C (10 mmHg) was collected, which was methyl laurate. Yield 70%.

(2) Synthesis of Sodium Laurate. The NaOH (1.96 g, 0.049mol) dissolved 100 ml ethanol was added into 500 ml three-necked flask. After the mixtue was heated to 70 °C and transformed into a clear solution, methyl laurate (10.0g, 0.046 mol) was added into this three-necked flask. The mixture were stirred at 70 °C for 5 hours under condensed reflux. After cooling, the mixture was evaporated under reduced pressure to remove ethanol and the residue was washed the mixture of methanol : H_2O 20:1 three time. The sodium laurate was obtained as a white solid after being dried under vacuum at 50 °C. Yield: 82.5%.

1.3 Synthesis of 3-bromo-N,N,N-trimethylpropan-1-aminium bromide

A mixture of 1,3-dibromopropane (100 g, 0.5 mol), trimethylamine in methanol (10 g, 0.05 mol, 30

%) and 500 ml acetone in a three-necked flask was added into a 1000 mL single-necked flask and was stirred at 25 °C for 6 hours under condensed reflux. After the reaction, suction filtration to obtain a white solid, which is 3-bromo-N,N,N-trimethylpropan-1-aminium bromide. Yield: 55.6 %.

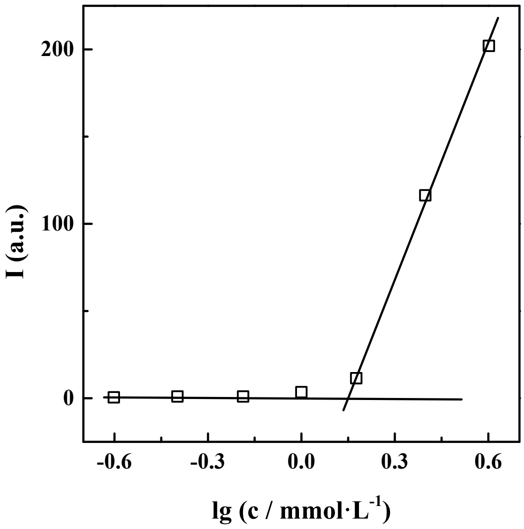


Fig. S4 Variations of the fluorescence intensity of the Nile red at 625 nm with the R-11-3-DA concentrations (25 °C)

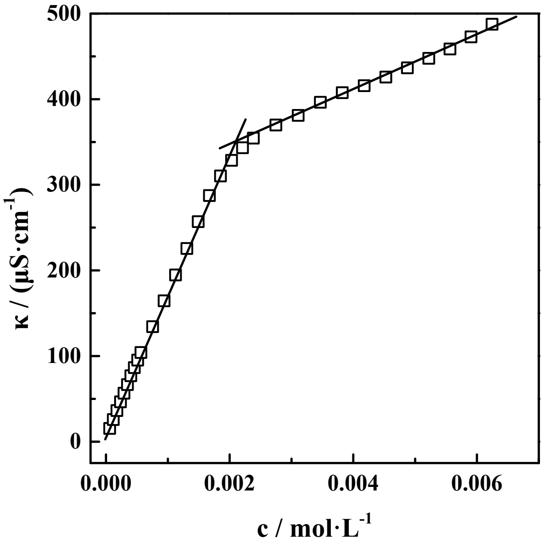


Fig. S5 Variations of the electrical conductivity with the R-11-3-DA concentrations (25 °C)

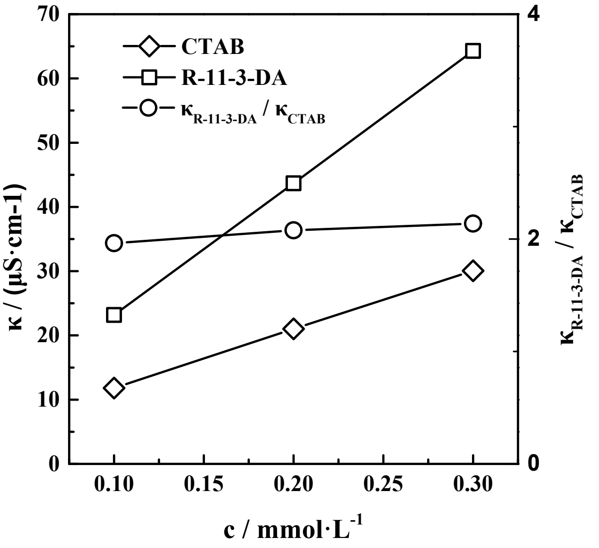


Fig.S6 Variations of the electrical conductivity with the R-11-3-DA or CTAB concentration at 25 °C

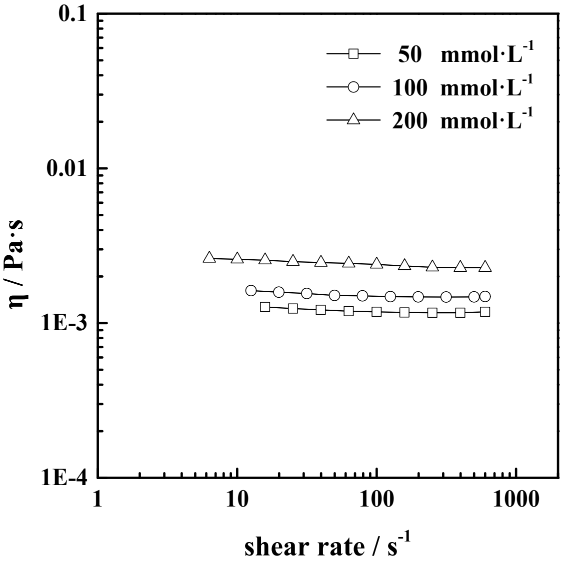


Fig. S7 Viscosity of R-11-3-DA solutions of different concentrations as a function of shear rate at 25 °C

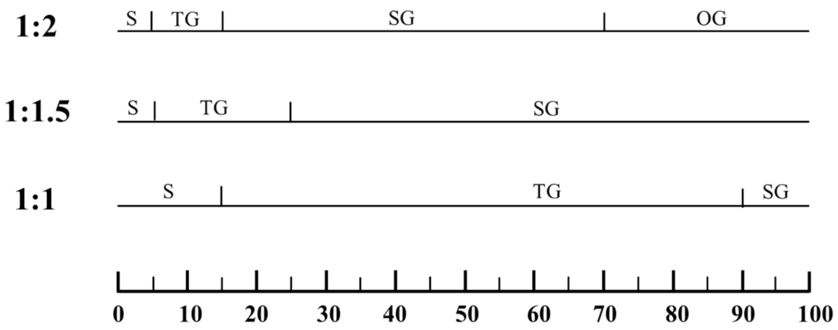


Fig. S8 Simple phase behavior of R-11-3-DA and SL mixed solutions with different molar ratio (25 °C)

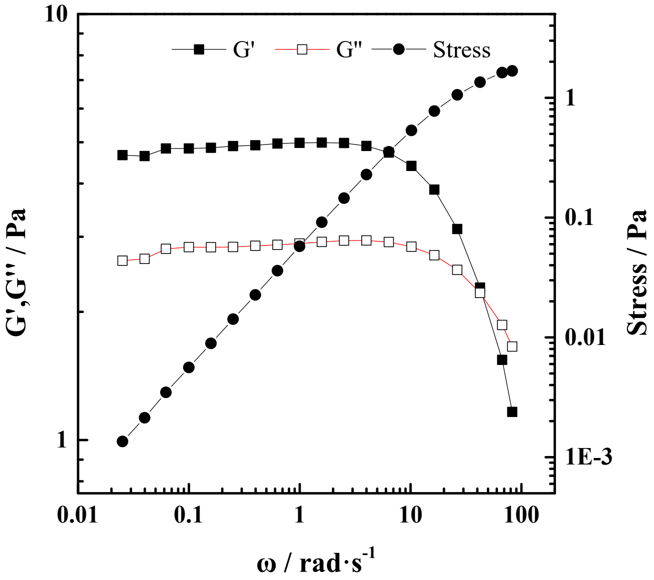


Fig. S9 Variation of storage modulus G'(■), loss modulus G''(□) and stress(●)with strain for 1:1.5 R-11-3-DA : SL mixed solution with 10 mmol·L^{-1} R-11-3-DA at 25 °C

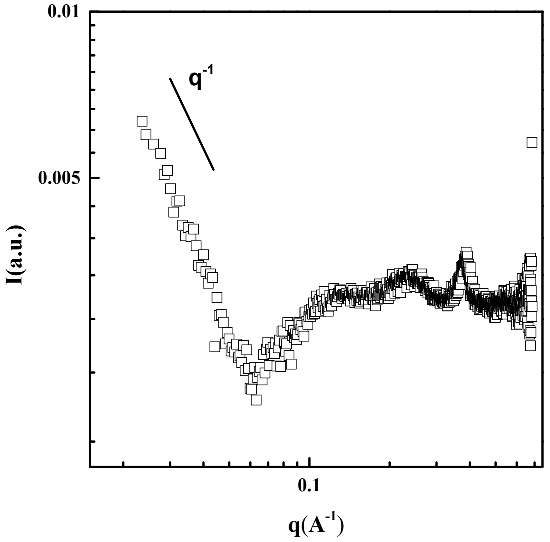


Fig. S10 SAXS protocol of 10 mmol·L^{-1} 1:1.5 R-11-3-DA:SL solution measured at 25 °C

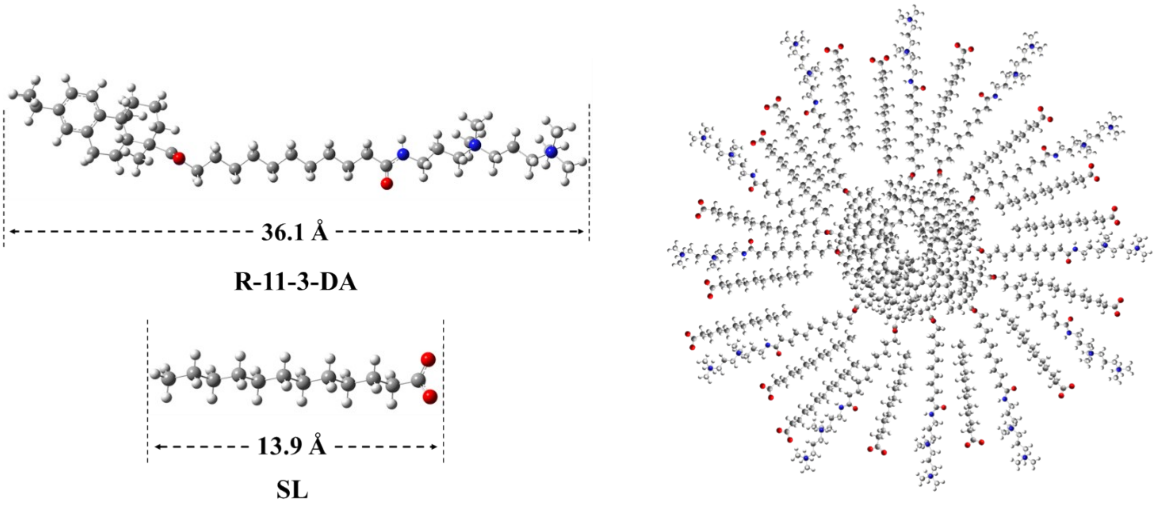


Fig. S11 The molecular length of R-11-3-DA and SL molecules and the molecular packing pattern at fiber interface