Crosslinked Poly(ionic liquid)s Enabled with Dication Ionic Liquid Moieties: Adaptable Lubricant Performance for Severe and Electric Field Conditions

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1.1 Synthesis of two-component quaternary ammonium salts

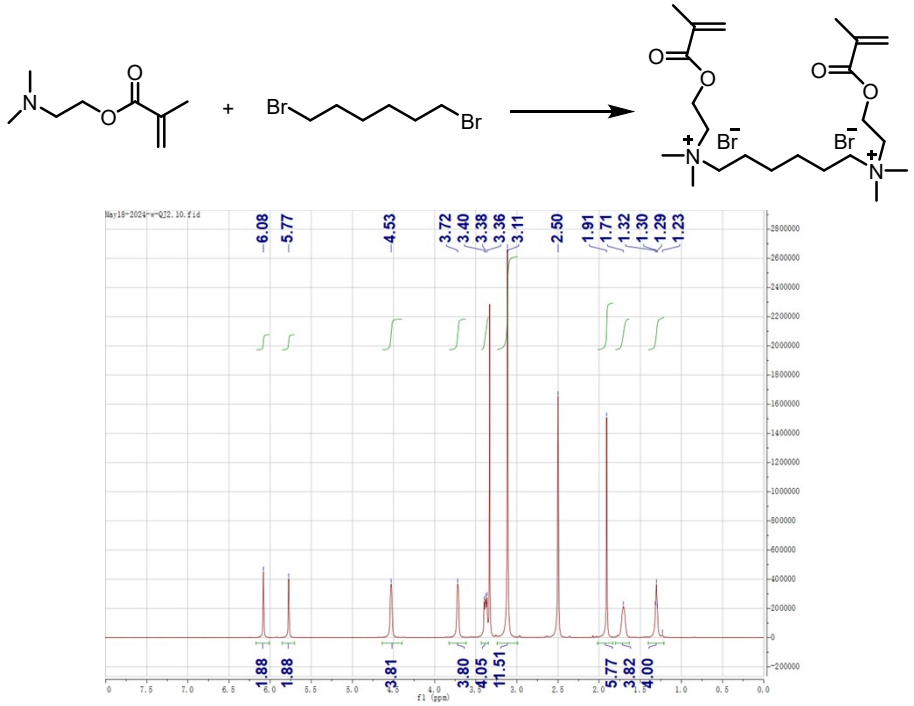


Figure S1. Synthesis and ^{1}H NMR spectra of two-component quaternary ammonium salts

A mixture of 40.87 g (260 mmol) of dimethylaminoethyl methacrylate and 24.4 g (100 mmol) of 1, 6-dibromohexane was added to a 500 mL round-bottom flask. Acetonitrile (1 mol/L) was used as the reaction solvent. The reaction was magnetically stirred at 50 °C for 48 h. After completion, the mixture was cooled to room temperature, washed with acetonitrile, filtered, and dried to afford 52 g of a white solid (yield: 93%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.08 (s, 2H), 5.77 (s, 2H), 4.53 (s, 4H), 3.72 (s, 4H), 3.43-3.35 (m, 4H), 3.11 (s, 12H), 1.91 (s, 6H), 1.71 (s, 4H), 1.31 (d, J = 6.1 Hz, 4H).

1.2 Synthesis of NP_{i8}-6-NP_{i8} ion monomers

6.45 g (20 mmol) of di(2-ethylhexyl) phosphate, and 0.8 g (20 mmol) of sodium hydroxide was added to a 100 mL round-bottom flask. Deionized water (1 mol/L) was used as the reaction solvent. After 6 h, 5.58 g (10 mmol) of the previously prepared two-component quaternary ammonium was added to, then the resulted reaction mixture was carried out at room temperature for 24 h. After completion, the product was extracted with dichloromethane and the solvent was removed by vacuum distillation. A total of 9.21 g of a white, transparent, viscous liquid was obtained (yield: 89%). ^{1}H NMR (500 MHz, Chloroform-d) δ 6.10 (s, 2H), 5.62 (s, 2H), 4.59 (s, 4H), 3.82 (s, 4H), 3.63 (s, 8H), 3.52-3.40 (m, 4H), 3.23 (s, 12H), 1.91 (s, 6H), 1.85 (s, 4H), 1.48-1.41 (m, 8H), 1.39 -1.33 (m, 4H), 1.28-1.20 (m, 28H), 0.86-0.82 (m, 24H).

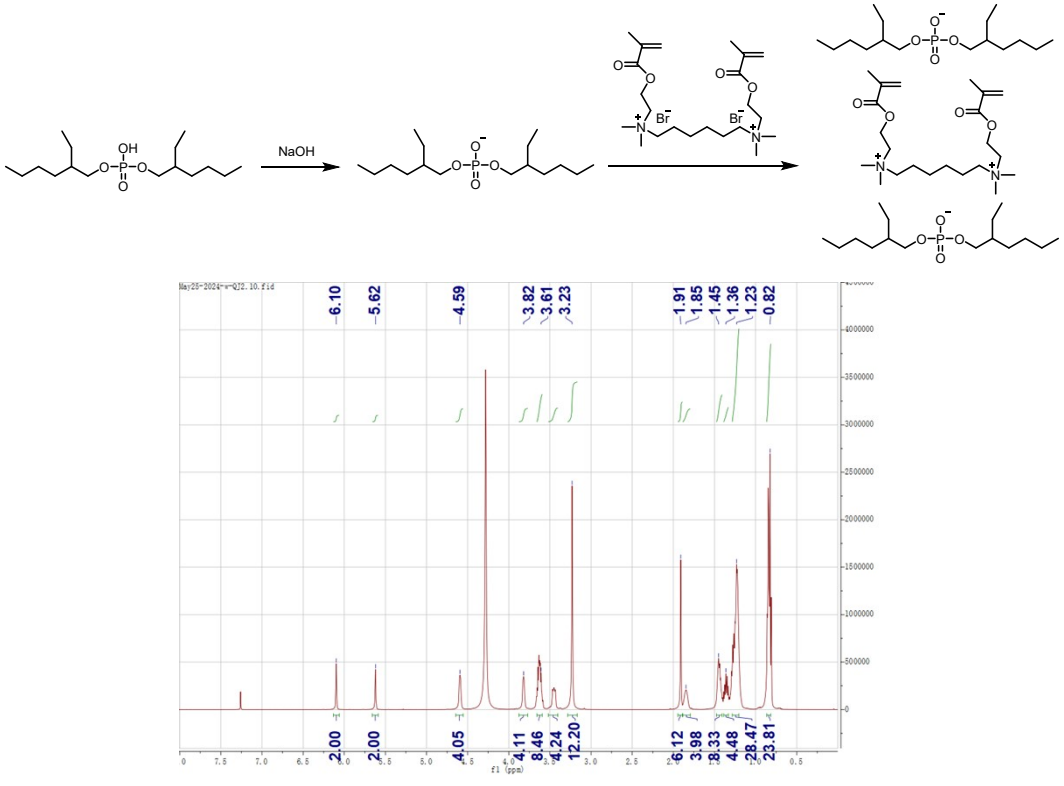


Figure S2. Synthesis and ^{1}H NMR spectra of NP_{i8}-6-NP_{i8} ion monomers

1.3 Synthesis of PS(NP_{i8}-6-NP_{i8}) copolymers

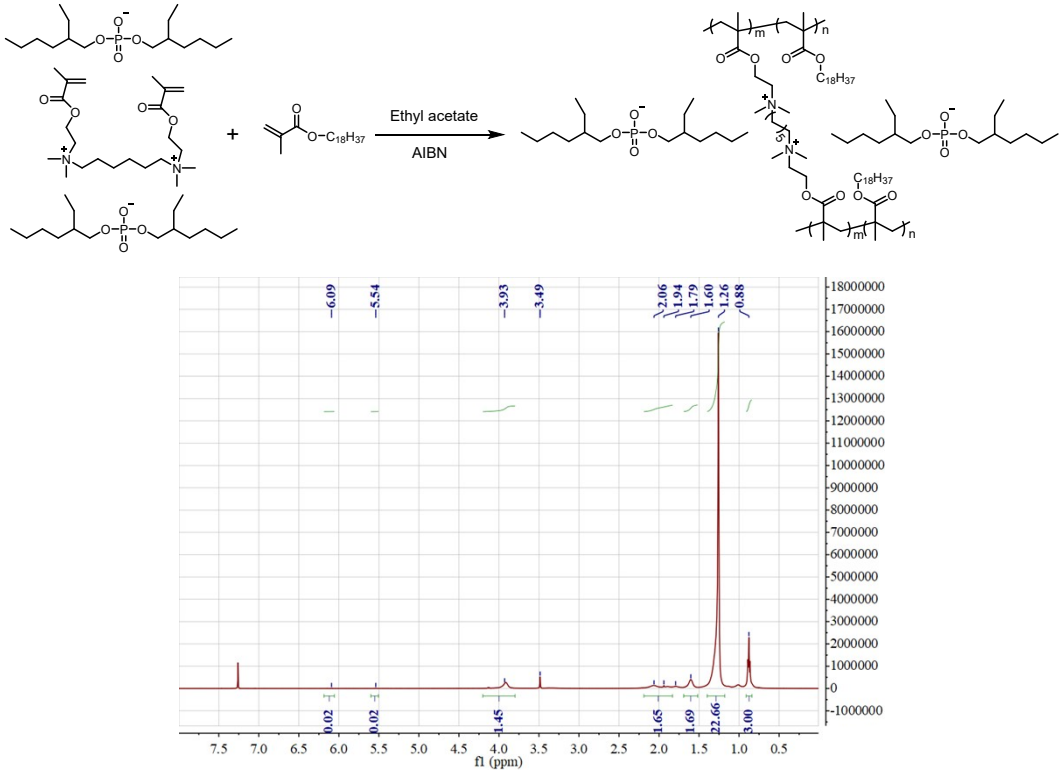


Figure S3. Synthesis and ^{1}H NMR spectra of PS(NP_{i8}-6-NP_{i8}) copolymers

A mixture of NP_{i8}-6-NP_{i8} ion monomer (5.21 g, 5 mmol) and stearyl methacrylate (16.93 g, 50 mmol) in a

molar ratio of 1:10 was dissolved in ethyl acetate (0.5 mol/L) with 1.5 mol% AIBN as the initiator. The reaction was carried out at 80 °C for 8 h under a nitrogen atmosphere. After completion, the crude product was recrystallized from methanol, filtered, and dried to yield 14.9 g of a white solid (yield: 67.3%).

2 The synthesis of PS(NSP_8-6-NSP_8) copolymers

2.1 Synthesis of O, O-dioctyl phosphorodithioate

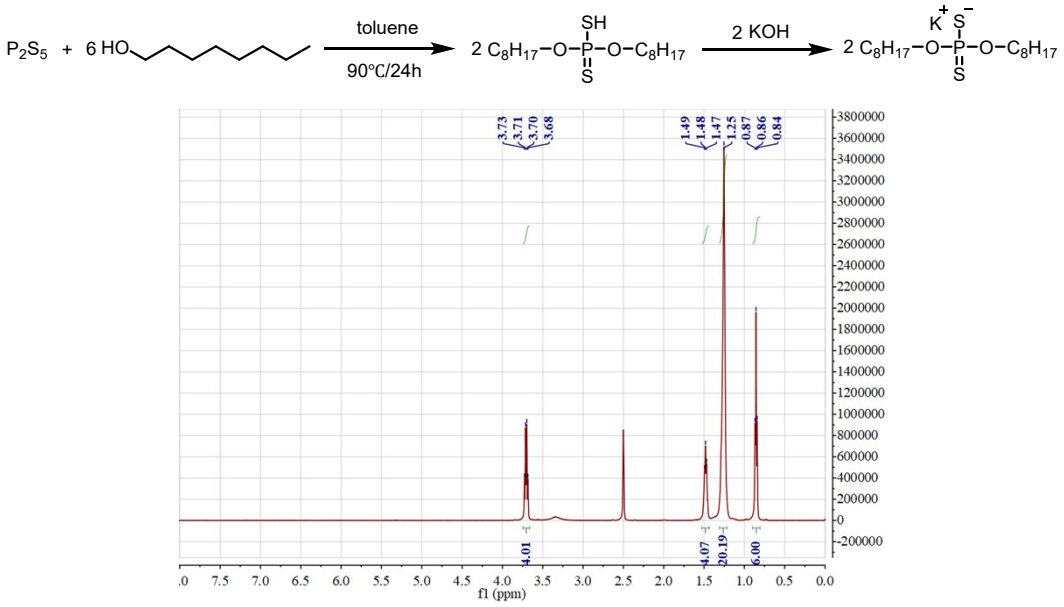


Figure S4. Synthesis and ^{1}H NMR spectra of O, O-dioctyl phosphorodithioate

A mixture of diphosphorus pentasulfide (11.11 g, 50 mmol) and n-octanol (39.06 g, 300 mmol) in a molar ratio of 1:6 was dissolved in toluene (1 mol/L) and reacted at 90 °C for 24 h. The mixture was cooled to room temperature and filtered. Potassium hydroxide solution (50wt%, 100 mmol) was then added dropwise to the filtrate. The mixture was stirred continuously at room temperature for 3 h. The solvent was removed by vacuum distillation. The crude product was washed with petroleum ether, filtered, and dried to yield 26.4 g of a white solid (yield: 67.2%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.71 (q, J = 6.9 Hz, 4H), 1.57-1.43 (m, 4H), 1.26 (q, J = 5.4, 4.7 Hz, 20H), 0.85 (t, J = 6.6 Hz, 6H).

2.2 **Synthesis of NSP_8-6-NSP_8 ion monomers**

A mixture of the previously synthesized two-component quaternary ammonium salt (5.58 g, 10 mmol) and O, O-dioctyl phosphorodithioate (7.85 g, 20 mmol) was added to a 100 mL round-bottom flask. Deionized water (1 mol/L) was used as the solvent. The mixture was stirred at room temperature for 24 h. After the reaction, the product was extracted with dichloromethane, and the solvent was removed by vacuum distillation. A white viscous solid (10 g) was obtained (yield: 90.5%). ^{1}H NMR (500 MHz, Chloroform-d) δ 6.13 (s, 2H), 5.66 (s, 2H), 4.64 (s, 4H), 4.05 (s, 4H), 3.89 (q, J = 7.3 Hz, 8H), 3.82 – 3.74 (m, 4H), 3.38 (s, 12H), 1.94 (s, 6H), 1.79 (s, 2H), 1.71 (dt,

J = 14.2, 6.8 Hz, 2H), 1.60 (t, J = 7.1 Hz, 12H), 1.24 (s, 50H), 0.86 (t, J = 6.7 Hz, 14H).

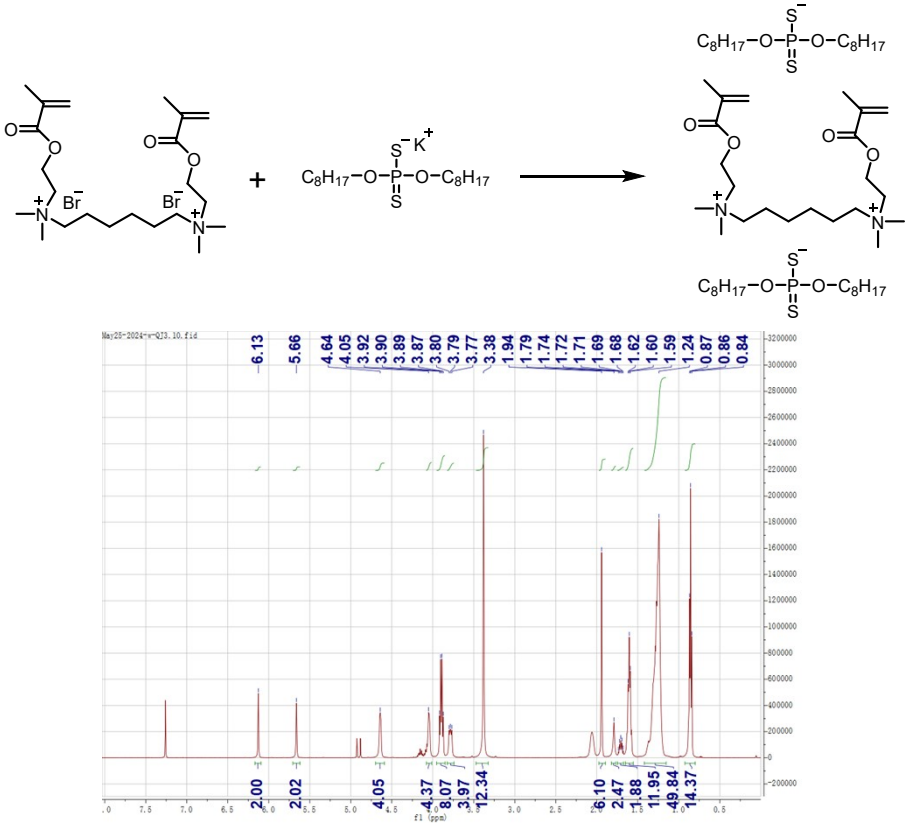


Figure S5. Synthesis and ^{1}H NMR spectra of NSP_8-6-NSP_8 ion monomers

2.3 **Synthesis of PS(NSP_8-6-NSP_8) copolymers**

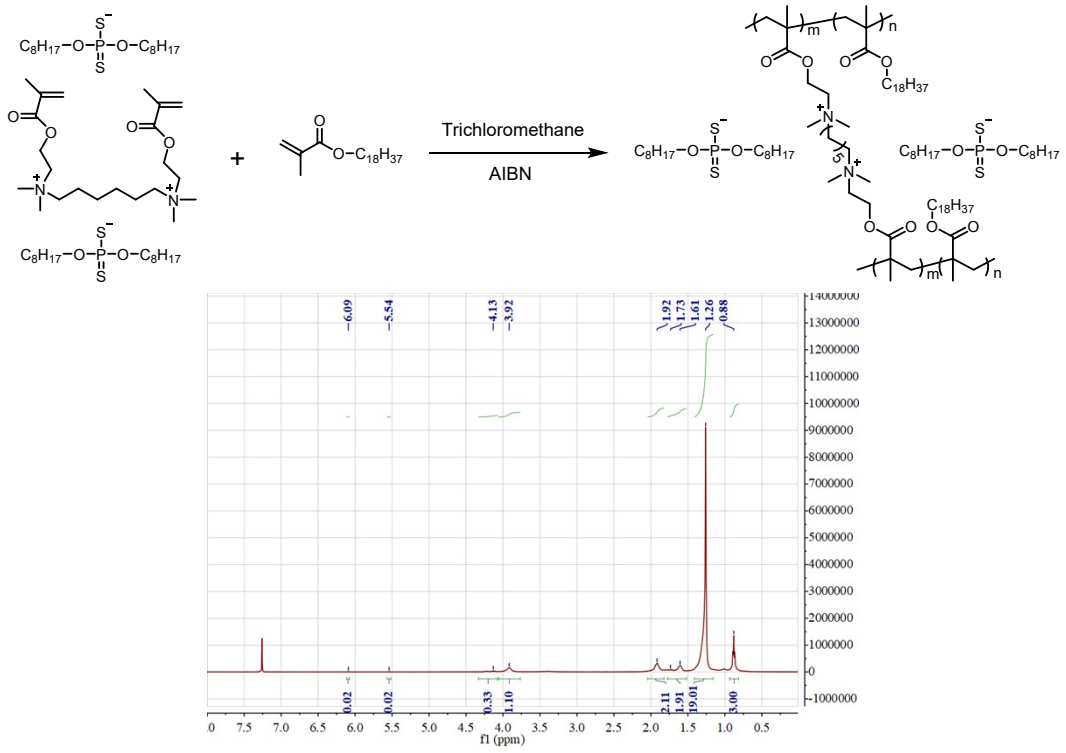


Figure S6. Synthesis and ^{1}H NMR spectra of PS(NSP_8-6-NSP_8) copolymers

A mixture of NSP_8-6-NSP_8 ion monomer (5.53 g, 5 mmol) and stearyl methacrylate (16.93 g, 50 mmol) at a molar ratio of 1:10 was dissolved in 0.3 mol/L chloroform. AIBN (1 mol%) was added as the initiator, and the reaction was carried out at 80 °C for 8 h under a nitrogen atmosphere. After the reaction, the solvent was removed by rotary evaporation. The residue was dissolved in a small amount of dichloromethane and recrystallized using cold methanol. The resulting solid was washed, filtered, and dried to yield 14 g of white powder (yield: 62.3%).

3 The synthesis of PS(NSP_{12}-6-NSP_{12}) copolymers

3.1 Synthesis of O, O-didodecyl phosphorodithioate

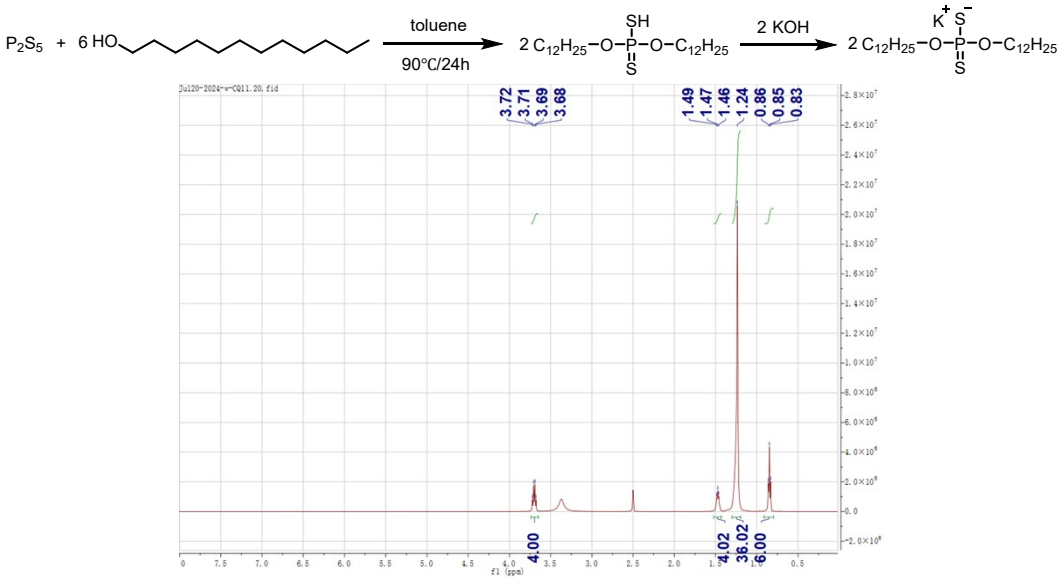


Figure S7. Synthesis and ^{1}H NMR spectra of O, O-didodecyl phosphorodithioate

A mixture of diphosphorus pentasulfide (11.11 g, 50 mmol) and dodecyl alcohol (55.9 g, 300 mmol) in a molar ratio of 1:6 was dissolved in toluene (1 mol/L) and reacted at 90 °C for 24 h. The reaction mixture was cooled to room temperature and filtered. Potassium hydroxide solution (50wt%, 100 mmol) was then added dropwise to the filtrate. The mixture was stirred continuously at room temperature for 3 h. The solvent was removed by vacuum distillation. The crude product was washed with petroleum ether, filtered, and dried to yield 35 g of a white solid (yield: 69.3%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.70 (q, J = 6.7 Hz, 4H), 1.52-1.43 (m, 4H), 1.24 (s, 36H), 0.85 (t, J = 6.8 Hz, 6H).

3.2 Synthesis of NSP_{12}-6-NSP_{12} ion monomers

A mixture of the previously synthesized two-component quaternary ammonium salt (5.58 g, 10 mmol) and O, O-didodecyl phosphorodithioate (10.1 g, 20 mmol) was added to a 100 mL round-bottom flask. Deionized water (1 mol/L) was used as the solvent. The mixture was stirred at room temperature for 24 h. After the reaction, the product was extracted with dichloromethane, and the solvent was removed by vacuum distillation. A white viscous

solid (11.1 g) was obtained (yield: 83.4%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.12 (s, 2H), 5.65 (s, 2H), 4.64 (s, 4H), 4.07-4.02 (m, 4FH), 3.88 (q, J = 7.3 Hz, 8H), 3.76 (s, 4H), 3.37 (s, 12H), 2.12 (s, 4H), 2.03 (t, J = 7.9 Hz, 4H), 1.93 (s, 6H), 1.70 (p, J = 6.7 Hz, 4H), 1.60 (dd, J = 13.7, 6.6 Hz, 12H), 1.23 (d, J = 6.2 Hz, 100H), 0.86 (t, J = 6.7 Hz, 16H).

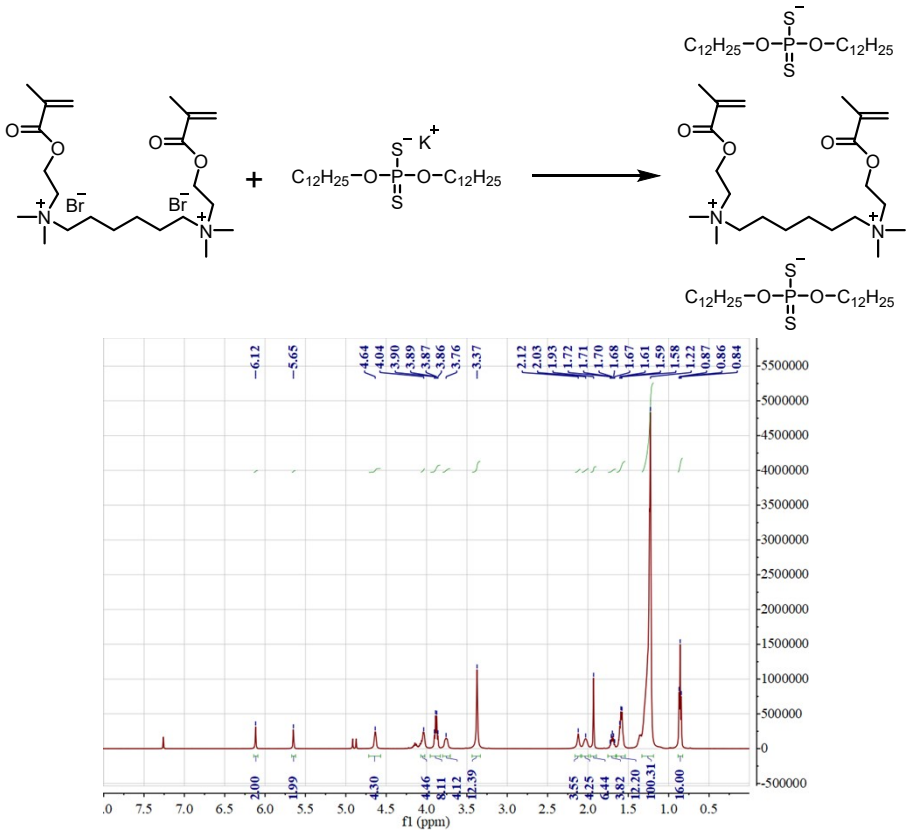
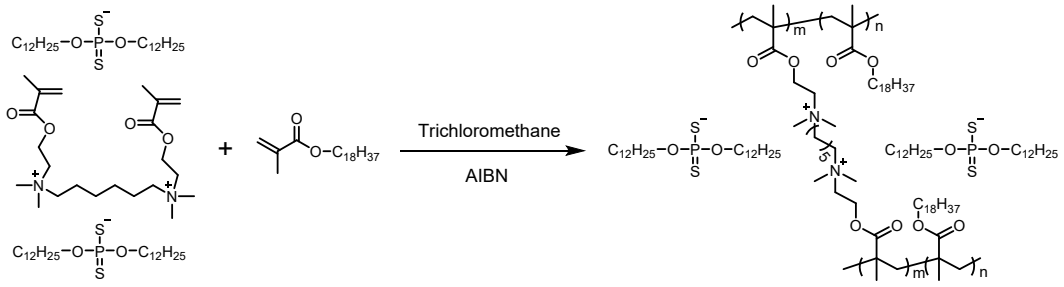


Figure S8. Synthesis and ^{1}H NMR spectra of NSP_{12}-6-NSP_{12} ion monomers

3.3 Synthesis of PS(NSP_{12}-6-NSP_{12}) copolymers

A mixture of NSP_{12}-6-NSP_{12} ion monomer (6.65 g, 5 mmol) and stearyl methacrylate (16.93 g, 50 mmol) at a molar ratio of 1:10 was dissolved in 0.3 mol/L chloroform. AIBN (1 mol%) was added as the initiator, and the reaction was carried out at 80 °C for 8 h under a nitrogen atmosphere. After the reaction, the solvent was removed by rotary evaporation. The residue was dissolved in a small amount of dichloromethane and recrystallized using cold methanol. The resulting solid was washed, filtered, and dried to yield 16.4 g of white powder (yield: 69.6%).



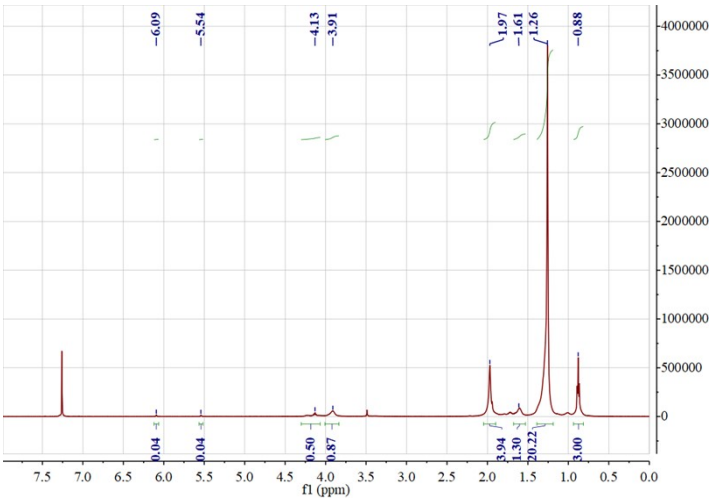


Figure S9. Synthesis and ^{1}H NMR spectra of PS(NSP$_{12}$-6-NSP$_{12}$) copolymers

4. TGA curves of the three PIL copolymers recorded in air

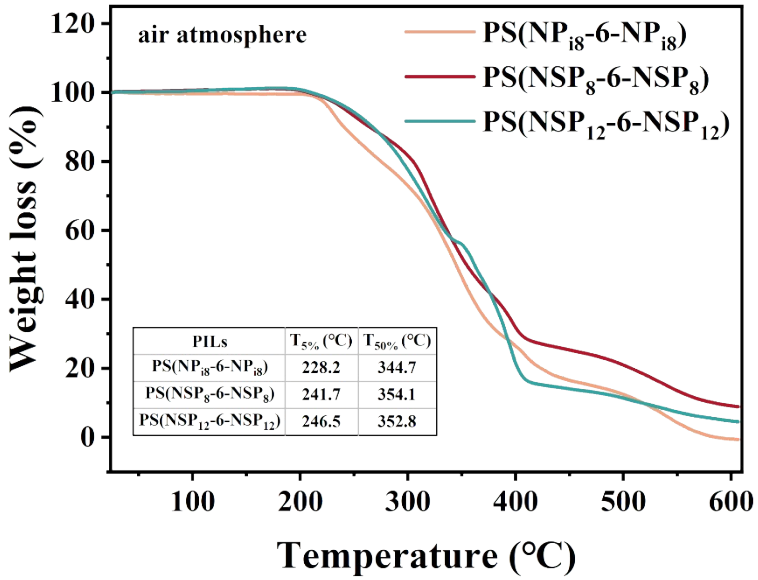


Figure S10. TGA curves of the three PIL copolymers recorded in air at a heating rate of 10 °C/min.

5. Testing of tribological properties under room temperature and 200N load

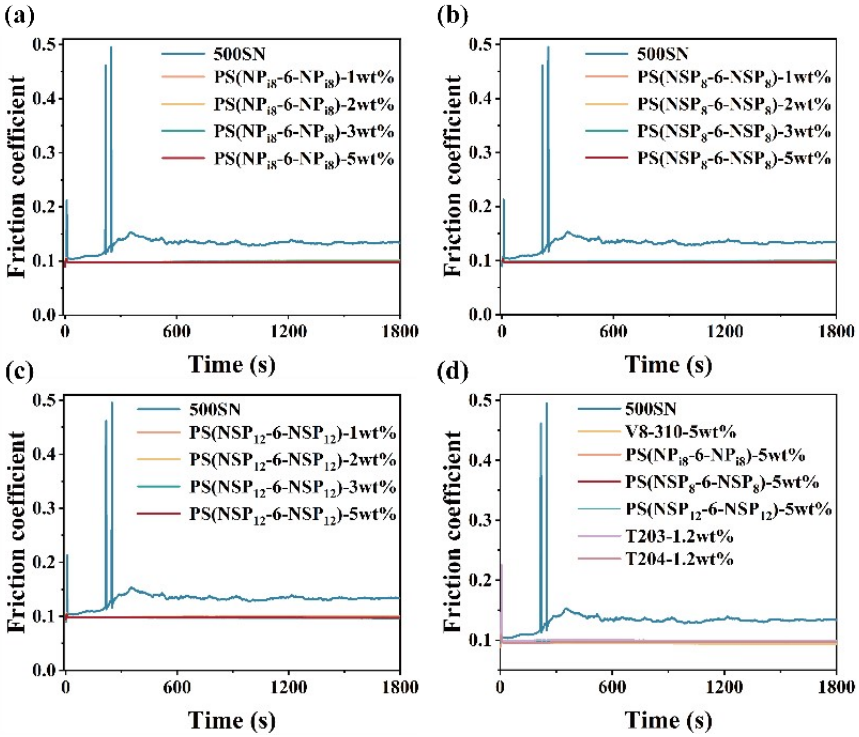


Figure S11. Friction coefficient profiles of 500SN copolymers with different concentrations at 200 N, 25 Hz, and room temperature PS(NP$_{i8}$-6-NP$_{i8}$) (a), PS(NSP$_8$-6-NSP$_8$) (b), PS(NSP$_{12}$-6-NSP$_{12}$) (c); 500SN blend containing 5 wt% additives (d).

6. Testing of tribological properties under varying conditions

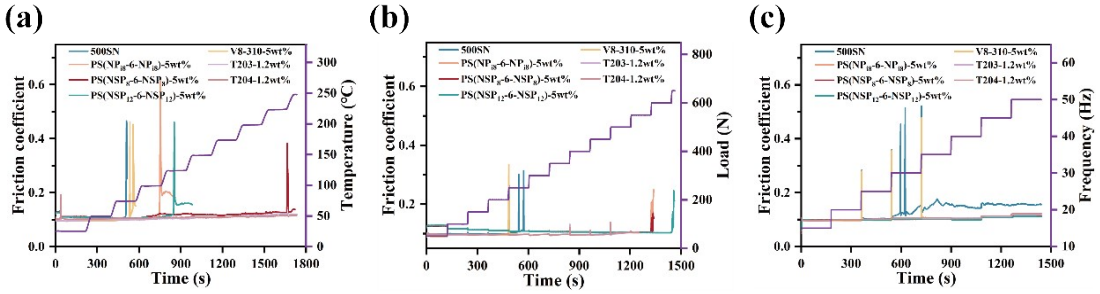


Figure S12. (a) The friction coefficient curves of 500SN blends with different copolymers under varied temperatures, (b) the extreme bearing capacity of 500SN blends, (c)the friction coefficient curves of 500SN blends with different copolymers under varied frequency.

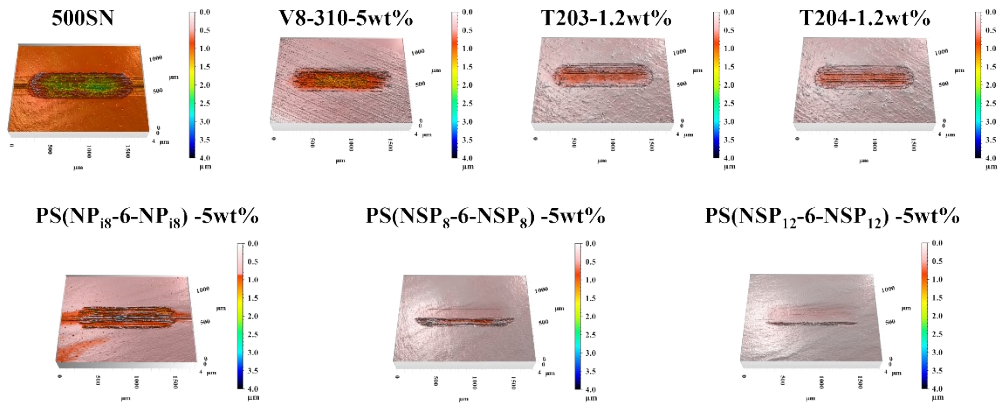


Figure S13. The 3D optical images of 500SN, 5 wt % copolymer, 5 wt % V8-310 and 1.2 wt % ZDDP worn surfaces obtained by SRV repeated experiments.

7. Frictional energy loss calculations for different lubricant systems

For a typical SRV contact under a normal load of $F_N = 200$ N, frequency $f = 25$ Hz, stroke amplitude $A = 1.0$ mm, and duration $t = 1800$ s, the average sliding velocity can be approximated as $v = 4Af = 0.1$ m/s.

The average friction between two mating surfaces $F = \mu F_N$,[1] thereby the total frictional energy dissipation is estimated by:

$$E = Pt = Fvt = \mu F_N vt$$

where E[2, 3] is the total frictional energy loss (J), μ is the steady-state friction coefficient, F_N is the applied load (N), P is the frictional power loss, v is the mean sliding velocity (m/s), and t is the test duration (s).

Using the measured friction coefficients:

500SN: $\mu = 0.13049$; PS(NSP$_{12}$-6-NSP$_{12}$): $\mu = 0.09857$

We calculate the frictional energy losses as follows:

500SN:

$$E_{500SN} = 0.13049 \times 200 \times 0.1 \times 1800 = 4.70 \times 10^3 \text{ J}$$

PS(NSP$_{12}$-6-NSP$_{12}$):

$$E_{PS(NSP12\text{ - }6\text{ - }NSP12)} = 0.09857 \times 200 \times 0.1 \times 1800 = 3.55 \times 10^3 \text{ J}$$

Thus, the mechanical energy loss is reduced by approximately 24.6% when using PS(NSP$_{12}$-6-NSP$_{12}$) compared to the base oil 500SN, corresponding to an energy saving of 1.15×10^3 J under identical conditions.

Table S1. Frictional energy loss calculations for different lubricant systems

Samples	μ	E (J)
500SN	0.13049	4.7×10^3
V8-310-5 wt%	0.09443	3.4×10^3
T203-1.2 wt%	0.09858	3.55×10^3
T204-1.2 wt%	0.09658	3.48×10^3
PS(NP_{i8}-6-NP_{i8}) -5 wt%	0.09882	3.56×10^3
PS(NSP_8-6-NSP_8) -5 wt%	0.09853	3.55×10^3
PS(NSP_{12}-6-NSP_{12}) -5 wt%	0.09857	3.55×10^3

8. Electric-field lubrication methodology and interpretation

In our experiments, a constant current of 1 A was supplied by an external DC power source. Although the power supply output is 48 V, the actual voltage measured at the ball-disk contact was consistently within the very low range of 0.1-0.3 V throughout the tests.

Using the Hertzian contact model (10 mm-diameter steel ball, 200 N load, AISI 52100 steel parameters: E = 210 GPa, v = 0.30), the estimated contact area and current density are:

Contact radius: [4, 5]

$a \approx 1.866 \times 10^{-4}$ m

Contact area:

$A_{\text{contact}} \approx 1.09 \times 10^{-7} m^2$

Average current density: [6]

$j = \frac{I}{A} \approx 9.14 \times 10^2 A\backslash cdotpcm^{-2}$

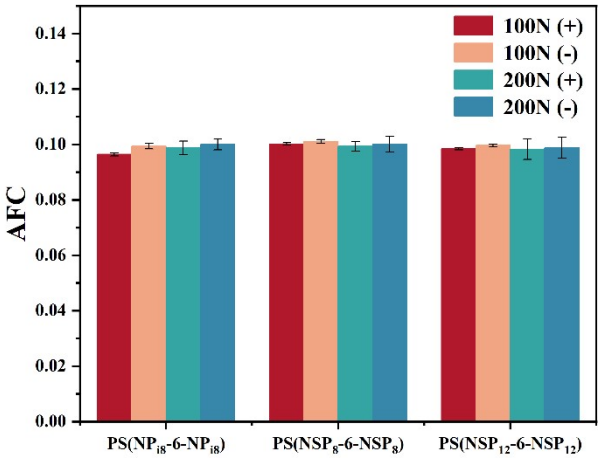


Figure S14. The influence of an external electric field on the tribological properties of lubricating oil containing 5 wt% copolymer. All COF values are presented as mean ± standard deviation (SD) from three independent tests (N = 3).

9. XPS and ToF-SIMS peak assignment and quantification

We have added the quantitative XPS atomic percentages for Fe, P, S, N, O, C, and other relevant elements obtained from the high-resolution spectra of the wear track (Table S2). The XPS probing area was selected at a representative central region of the wear scar. To support the representativeness of this location, the ToF-SIMS ion maps demonstrate that P^- and S^- containing species are uniformly distributed across the wear track, indicating spatial homogeneity of the tribofilm.

Table S2 The quantitative atomic percentage of XPS

Sample	(atomic %)					
	C	O	Fe	N	P	S
500SN	54.6	28.32	17.08	/	/	/
PS(NP$_{i8}$-6-NP$_{i8}$)	46.27	34.12	14.74	1.37	3.5	/
PS(NSP$_8$-6-NSP$_8$)	29.93	38.03	13.7	1.6	15.44	1.3
PS(NSP$_{12}$-6-NSP$_{12}$)	38.17	35.78	10.59	1.22	12.83	1.41

All XPS measurements were performed using a low-energy electron charge neutralizer to eliminate charging effects. Binding energies were calibrated using the C 1s (C–C/C–H) peak at 284.8 eV.

S 2p fitting: Spin-orbit splitting was fixed at 1.24 eV, with a 2:1 area ratio ($2p_{3/2}$: $2p_{1/2}$). Chemical states include sulfide species (S^{2-}, $2p_{3/2} \approx$ 161-162 eV) and sulfate/sulfoxy species ($2p_{3/2} \approx$ 168-170 eV).

P 2p fitting: Spin-orbit splitting was fixed at 0.9 eV, with a 2:1 peak area ratio. Peak positions were constrained within the literature ranges for phosphate/$FePO_4$ species (P $2p_{3/2} \approx$ 132.6-133.0 eV).

All regions were fitted using a Shirley background and GL-mixed peak functions (GL(30)), and the FWHM values were kept within consistent limits to avoid overfitting.

All XPS spectra used to support the chemical composition of the tribofilm are from the as-formed surfaces without any Ar^+ sputtering, to avoid possible reduction or alteration of S^- or P^- containing species.

10. Reference

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