Supporting Information

Highly Branched Polymethacrylates Prepared Efficiently: Brancher-Directed Topology and Application Performance

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1. Experimental Methods

General information. Unless stated otherwise, all manipulations with air- and moisture-sensitive chemicals and reagents were performed using standard Schlenk techniques on a dual-manifold line, or in an inert gas (N_2)-filled glovebox. All solvents and reagents were obtained from commercial sources and were purified according to standard procedures before use. Unless otherwise stated, the monomers and branchers were purchased and dried over activated CaH_2 overnight, followed by vacuum distillation and stored in bottles at −22 °C inside of a freezer. The paraffinic type base oil 150N was purchased by Formosa Plastics Corporation/Group. The paraffinic type base oil 150N that we employ belongs to solvent refined paraffinic mineral, with medium kinematic viscosities of 29.88 cSt (KV40 at 40 °C) and 5.09 cSt (KV100 at 100 °C), as well as a moderate VI of 96. These primary paraments make it ideal for evaluating the performance of VII. The sample TK-chem V6545 is a commercial VI improver based on a linear polymethacrylate, which is kindly donated by Dalian Xinyiye New Material Development Co., Ltd and employed here as a comparative example.

Identification of pendant double bonds by the spectra of isolated branched polymers: The chemical shifts of the double bond in the pendant methacrylate group are 6.17 ppm (s) and 5.44 ppm (m), while the chemical shifts of the double bond in the pendant styrene group are reported to be 5.15-5.25 (d, =CH ~ trans to benzyl), 5.65-5.75 (d, =CH ~ cis to benzyl) and 6.5-6.8 (m, =CH ~ to benzyl).[1] In the ^{1}H NMR spectra of PEHMA$_{50}$-EGDMA$_{1.0}$ and PEHMA$_{50}$-VBMA$_{1.0}$, the signals attributed to the double bond in the pendant methacrylate group are clearly observed. While for the ^{1}H NMR spectra of PEHMA$_{50}$-DVB$_{0.75}$ and PEHMA$_{50}$-VBMA$_{1.0}$, there is no signal at the chemical shifts of the double bond in the pendant styrene group. Besides, the signals at 5.54-5.59 ppm and 5.18-5.24 ppm are assigned to the residual SaBOX ligands. These results demonstrates that some pendant double bonds are reserved in PEHMA$_{50}$-EGDMA$_{1.0}$, the remaining pendant double bonds of VBMA units in PEHMA$_{50}$-VBMA$_{1.0}$ are all on the methacrylate side, and no pendant double bonds is retained in PEHMA$_{50}$-DVB$_{0.75}$.

Calculations of monomer conversion and the content of pendant double bonds[1]: The polymerization process was tracked. Both the monomer conversion and the remaining amount of pendant double bonds are calculated based on the quantitative ^{1}H NMR spectrum of the polymerization mixture, using DMSO and mesitylene as internal standards, respectively. Although the signals of free monomers and pendant double bond overlap, they can still be distinguished. The chemical shifts of double bonds in free monomer are 6.09 ppm and 5.54 ppm, those for the methacrylate double bonds of divinyl branchers (VBMA and EGDMA) are 6.15 ppm and 5.58 ppm, and those of pendant double bonds are 6.17 ppm, 5.43-5.50 ppm. GSD fitting of multipeak splitting was performed by Mestrenova. The monomer conversion (conv.(monomer) is calculated based on the formula ($I_{\text{monomer double bond}}$ and I_{DMSO} represent the integral area of signal peak of at 6.09 and 2.62, respectively):

$$conv.\,(monomer) = \frac{\left(I_{monomer\ double\ bond}/I_{DMSO}\right)_0 - \left(I_{monomer\ double\ bond}/I_{DMSO}\right)_t}{\left(I_{monomer\ double\ bond}/I_{DMSO}\right)_0} \times 100\%$$

The remaining amount of pendant double bonds (f_{p}) is calculated based on the formula[2]:

$$f_p = \frac{\left(I_{pendant\ double\ bond}/I_{mesitylene}\right)_t}{\left(I_{brancher}/I_{mesitylene}\right)_0} \times 100\%$$

$I_{\text{pendant double bond}}$, I_{brancher} and $I_{\text{mesitylene}}$ represent the integral area of signal peak at 6.17 ppm, 6.15 ppm, and 6.80 ppm, respectively. It should be noted that there should be a great error in the calculation of f_{p} because of the overlapped and weak signals of pendant double bond.

Synthesis of *p*-divinylbenzene (DVB).[3] Methyltriphenyl phosphonium bromide (0.11 mol, 39.294 g), terephtalic aldehyde (0.05 mol, 6.706 g) and potassium carbonate (0.11 mol, 15.203 g) were dissolved in 1,4-dioxane (100 ml) containing water (1.5 ml). The reaction mixture was stirred and refluxed for 10 h in argon atmosphere. After cooled to room temperature, the system was filtered with pentane. The resulting crude product was purified by chromatography over a silica gel column, using 1 vol.% Et_2O/hexane as eluent. DVB (2.141 g, 0.016 mol) was obtained in 33% yield as white solid and stored at −22 °C inside of a freezer. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (s, 4H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 2H), 5.75 (dd, *J* = 17.6 Hz, 0.9 Hz, 2H), 5.24 (dd, *J* = 10.9 Hz, 0.9 Hz, 2H). **Note:** DVB was easily removed during the concentration by vacuum pump at room temperature because of its melting point nearby 30 ^{o}C and low boiling point, which leads to a low yield.

Synthesis of *p*-vinylbenzyl methacrylate (VBMA).[1] *p*-Chloromethylstyrene (0.07 mol, 10 ml) was added dropwise to an ice-cooled solution of sodium methacrylate and tetrabutylammonium hydrogen sufate (TBAH) (0.01 mol, 3.395 g) in THF/DMSO (v/v = 7/1, 240 ml). The mixture was stirred at 60 ^{o}C overnight. The resulting orange liquid was poured into water and extracted with chloroform three times. The organic phase was washed several times with water and dried over sodium sulfate overnight. After filtration, the solvent was removed on a rotavapor at room temperature, and the crude product was further purified by chromatography over a silica gel column, using dichloromethane/hexane as eluent. VBMA (11.887 g, 0.063 mol) was obtained in 90% yield as a colorless liquid and stored at −22 °C inside of a freezer after removing oxygen. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.15 (s, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.59 (s, 1H), 5.26 (d, *J* = 10.8 Hz, 1H), 5.18 (s, 2H), 1.97 (s, 3H).

Synthesis of branched polymethacrylates (General ATRcP procedure). All polymerizations were set up and performed under an atmosphere of oxygen-free, dry argon using standard Schlenk-line techniques or inside a nitrogen-filled glovebox. In an ampule equipped with a magnetic stirrer bar, a mixture of $CuBr_2$, ligand and Cu(0) powder in solvent was stirred at room temperature for 2 h under the atmosphere of nitrogen. After that, monomer, brancher and initiator were added into the ampule. The ampules were placed at a certain temperature. After stirring for the allotted period of time, an aliquot (1.0 mL) was removed and quenched with THF. Conversion was determined by integration of the monomer vs. internal standard (DMSO) in the ^{1}H NMR spectrum of the reaction mixture. After the polymerization was completed, the contents of the ampules left were dissolved in

THF and the solution was filtered through a glass funnel with neutral alumina. The filtrate was concentrated under reduced pressure. The residuals were resolved with 0.5 mL THF. This solution was added to an approximately 30-fold excess of rapidly stirred MeOH/H_2O (v/v =9/1). The precipitate that formed was filtered and washed with MeOH. The precipitate was dried to constant weight in a vacuum oven.

Copolymerization of MMA and styrene (for the calculation of reactivity ratio). All the copolymerizations of MMA and styrene were set up and performed under an atmosphere of oxygen-free, dry argon using standard Schlenk-line techniques or inside a nitrogen-filled glovebox. In an ampule equipped with a magnetic stirrer bar, a mixture of $CuBr_2$, ligand and Cu(0) powder in solvent was stirred at room temperature for 2 h under the atmosphere of nitrogen. After that, the required weight of MMA, styrene and initiator were added into the ampule. The ampules were placed at 30 ^{o}C. After stirring for the allotted period of time, an aliquot (1.0 mL) was removed and quenched with THF. Conversion was determined by integration of the monomer vs. internal standard (DMSO) in the ^{1}H NMR spectrum of the reaction mixture. The conversion of either MMA or styrene was kept below 20%. After the polymerization was completed, the contents of the ampules left were dissolved in THF and the solution was filtered through a glass funnel with neutral alumina. The filtrate was concentrated under reduced pressure. The residuals were resolved with 0.5 mL THF. This solution was added to an approximately 30-fold excess of rapidly stirred *n*-pentane. The precipitate that formed was filtered and washed with *n*-pentane. The precipitate was dried to constant weight in a vacuum oven.

Polymer characterization. ^{1}H NMR spectra were recorded on Varian 400 MHz spectrometer and Agilent Technologies 400 MHz spectrometer. The relative molecular weight (MW_{RI}) and dispersity ($Đ_{RI}$) were measured by gel permeation chromatography (GPC) with a Waters 2414 differential refractive index (RI) detector, equipped with HR-3, HR-4, HR-5 columns in series. The analysis was undertaken at 35 ^{o}C with purified high-performance-liquid-chromatography-grade THF as the eluent at the rate of 1 ml/min. Calibration was performed with standard PMMA. The absolute molecular weight (MW_{LS}) and dispersity ($Đ_{LS}$) and intrinsic viscosity ([η]) were measured at 35 °C by Wyatt instrument equipped with a DAWN EOS multi-angle laser light scattering (MALLS with 18 angles) detector (Wyatt Technology) , a T-rEX refractive index detector (Wyatt S6 Technology) and a Wyatt Visco Star viscometer detector (VD), and connected with two PL gel MIXED-B columns. HPLC-grade THF with a flow rate of 1.0 mL/min was used as eluent. The refractive index increments (dn/dc) were determined using a Wyatt Optilab REX (λ = 662 nm) interferometric differential refractometer in batch mode, which showed values for PDMA 0.075 mL/g.

Lubricant formulation. Prescribed amounts of each polymethacrylate sample were blended into a base oil to prepare lubricants formulated with different polymers at various concentrations. The formulated lubricants were homogenized overnight using a mechanical shaker at 60 °C to obtain a uniform polymer dispersion in the lubricants. No additional additives other than the polymers were used in the lubricant formulation.

Lubricant performance testing. The KVs of the lubricants (both sheared and unsheared) at 40 and 100 °C were tested according to GB/T 265, and the VI values were calculated by GB/T 1995. Kurt Orbahn testing of the viscosity loss of the lubricants under shear was performed according to SH/T 0103. The tested lubricants were subjected to high shear flow through a European diesel injector apparatus, and their kinematic viscosities at 40 and 100 °C were monitored after 30 cycles to investigate shear degradation of the polymers. Shear degradation led to a drop of the polymer molecular weight and a loss in lubricant kinematic viscosity. Data were recorded after 30 cycles. The shear stability index was calculated after 30 cycles on the basis of ASTM D6022. Transmittance was measured by Varian Cary 100 Scan UV-Vis at 560 nm.

2. The Supplemental Figures

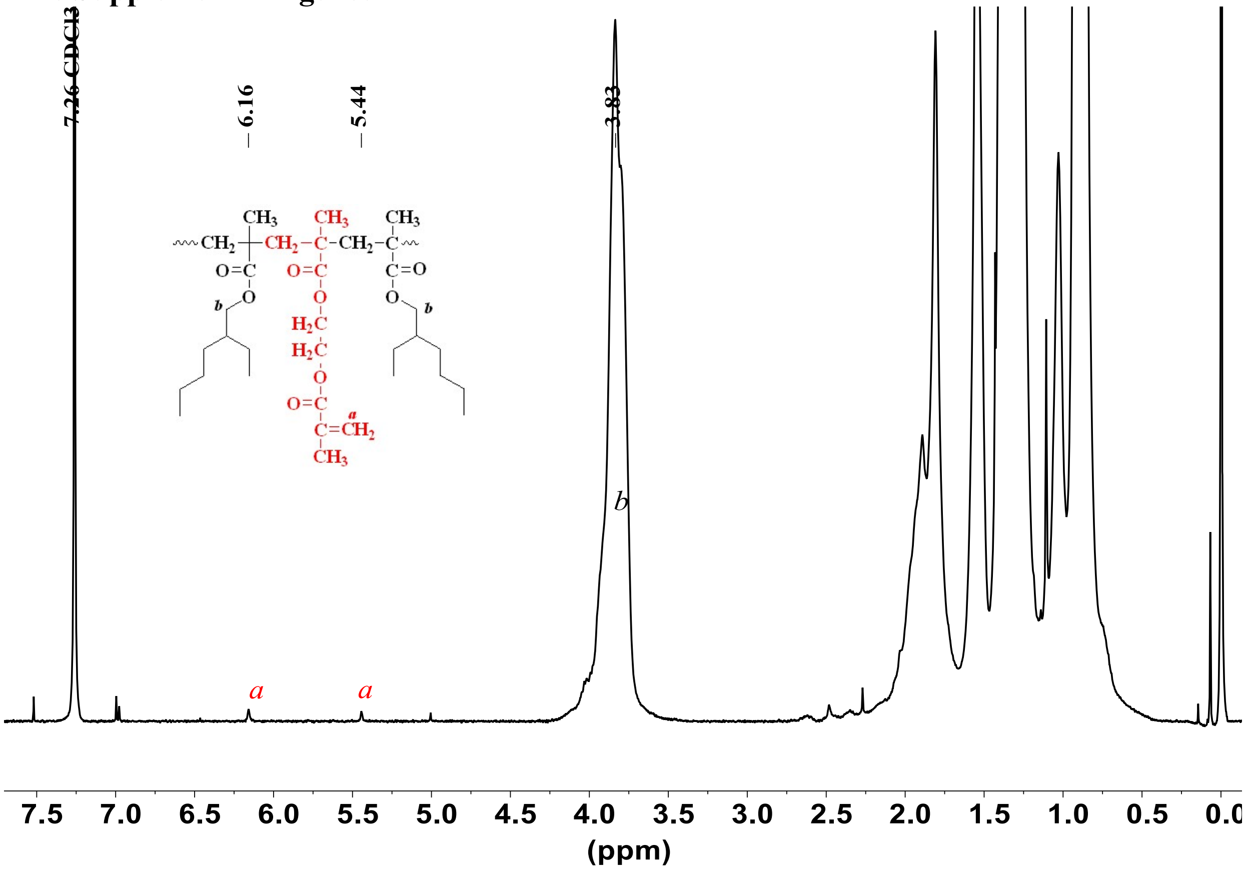

Figure S1. ^{1}H NMR spectrum of PEHMA$_{50}$-EGDMA$_{1.0}$.

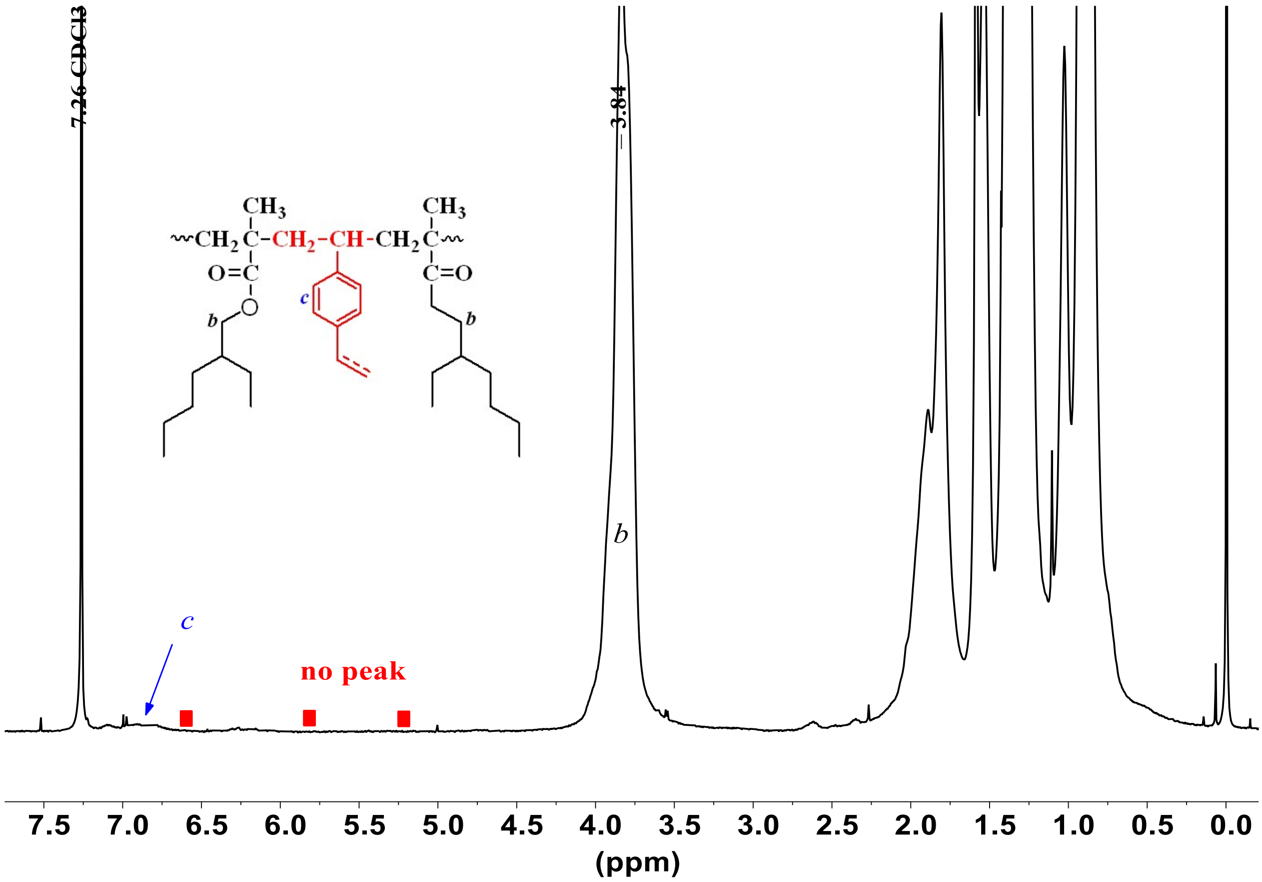

Figure S2. ^{1}H NMR spectrum of PEHMA$_{50}$-DVB$_{0.75}$.

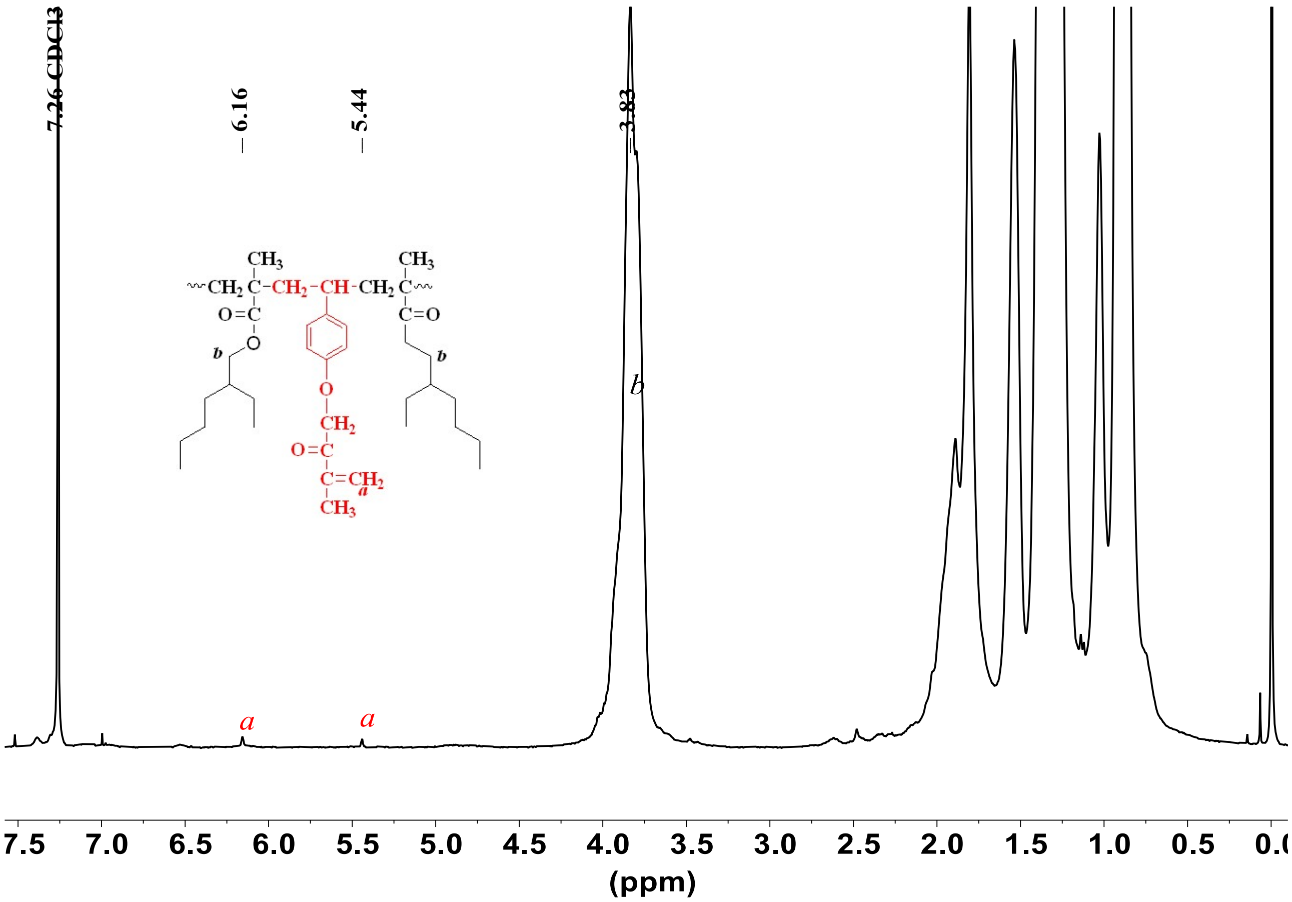

Figure S3. ^{1}H NMR spectrum of PEHMA$_{50}$-VBMA$_{1.0}$.

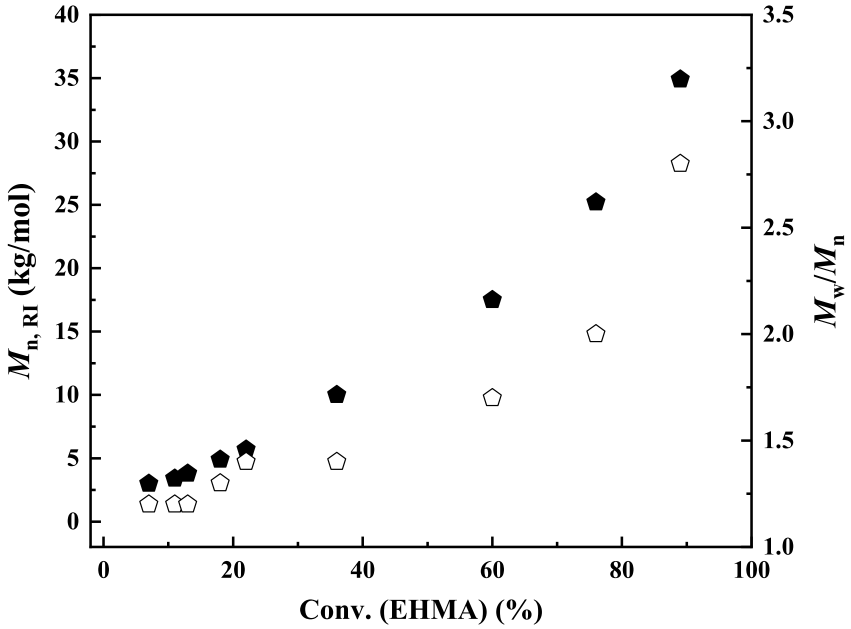

Figure S4. M_n (filled points) and M_w/M_n (unfilled points) versus conversion during the synthesis of PEHMA$_{50}$-DVB$_{0.75}$.

3. The Performance of Lubricants Formulated with Various Polymethacrylates

Table S1. Transmittance of lubricants formulated with various polymethacrylates

Sample	Transmittance
150 N base oil	99
150 N base oil + 1 wt % PEHMA$_{50}$-DVB$_{0.75}$ (I)	99
150 N base oil + 5 wt % PEHMA$_{50}$-DVB$_{0.75}$ (II)	95
150 N base oil + 1 wt % PEHMA$_{600}$ (III)	99
150 N base oil + 5 wt % PEHMA$_{600}$ (IV)	82

Table S2. Viscosity performance and shear stability of lubricants formulated with various polymethacrylates[a]

Polymethacrylate additive[b]	KV40 (cSt)	KV100 (cSt)	ΔKV100 (%)	VI	KV100 loss (%)	SSI	appearance	$T_{d,5}$[c]
None	29.88	5.088	–	96	–	0	clear	–
PEHMA$_{600}$ (1 wt%)	35.38	6.708	31.8	118	11.2	1.2	clear	249
PEHMA$_{600}$ (5 wt%)	65.55	11.19	119.9	165	–	–	hazy	249
PEHMA$_{50}$-EGDMA$_{1.0}$ (1 wt%)	32.02	5.608	10.2	114	-0.5	0.6	clear	268
PEHMA$_{50}$-EGDMA$_{1.0}$ (5 wt%)	41.34	7.224	42.0	138	–	–	hazy	268
PEHMA$_{50}$-DVB$_{0.75}$ (1 wt%)	32.59	5.732	12.7	117	-12.7	-0.7	clear	268
PEHMA$_{50}$-DVB$_{0.75}$ (5 wt%)	50.95	8.821	73.4	153	–	–	clear	268
PEHMA$_{50}$-VBMA$_{1.0}$ (1 wt%)	31.47	5.549	9.1	114	-1.4	0.0	clear	262
PEHMA$_{50}$-VBMA$_{1.0}$ (5 wt%)	41.93	6.983	37.2	126	–	–	clear	262
TK-chem V6545 (1 wt%)	33.85	13.3	12.1	108	24.5	7.0	clear	–
TK-chem V6545 (5 wt%)	41.60	39.2	45.8	145	–	–	clear	–

[a]The KVs of the lubricants (both sheared and unsheared) at 40 and 100 °C were tested according to GB/T 265, and the VI values were calculated by GB/T 1995. Kurt Orbahn testing of the viscosity loss of the lubricants under shear was performed according to SH/T 0103 using a European diesel injector apparatus. Data were recorded after 30 cycles. The shear stability index was calculated after 30 cycles on the basis of ASTM D6022. [b]Reaction condition for preparing the branched polymers: $n(\mathrm{CuBr_2})/n(\mathrm{Cu})/n(\mathrm{SaBOX})/n(\mathrm{methacrylate})/n(\mathrm{BPN})$ = 1/4/2/100/2, $n(\mathrm{methacrylate})/n(\mathrm{brancher})$ = 50/1, THF/DMSO (v/v = 7/1) was used as the solvent, at 30 °C, 72 h, conv.(methacrylate) > 99%. Different from the reactions in Table 1, tracing is not carried out. [c]5% weight loss temperature of the polymethacrylates determined by TGA.

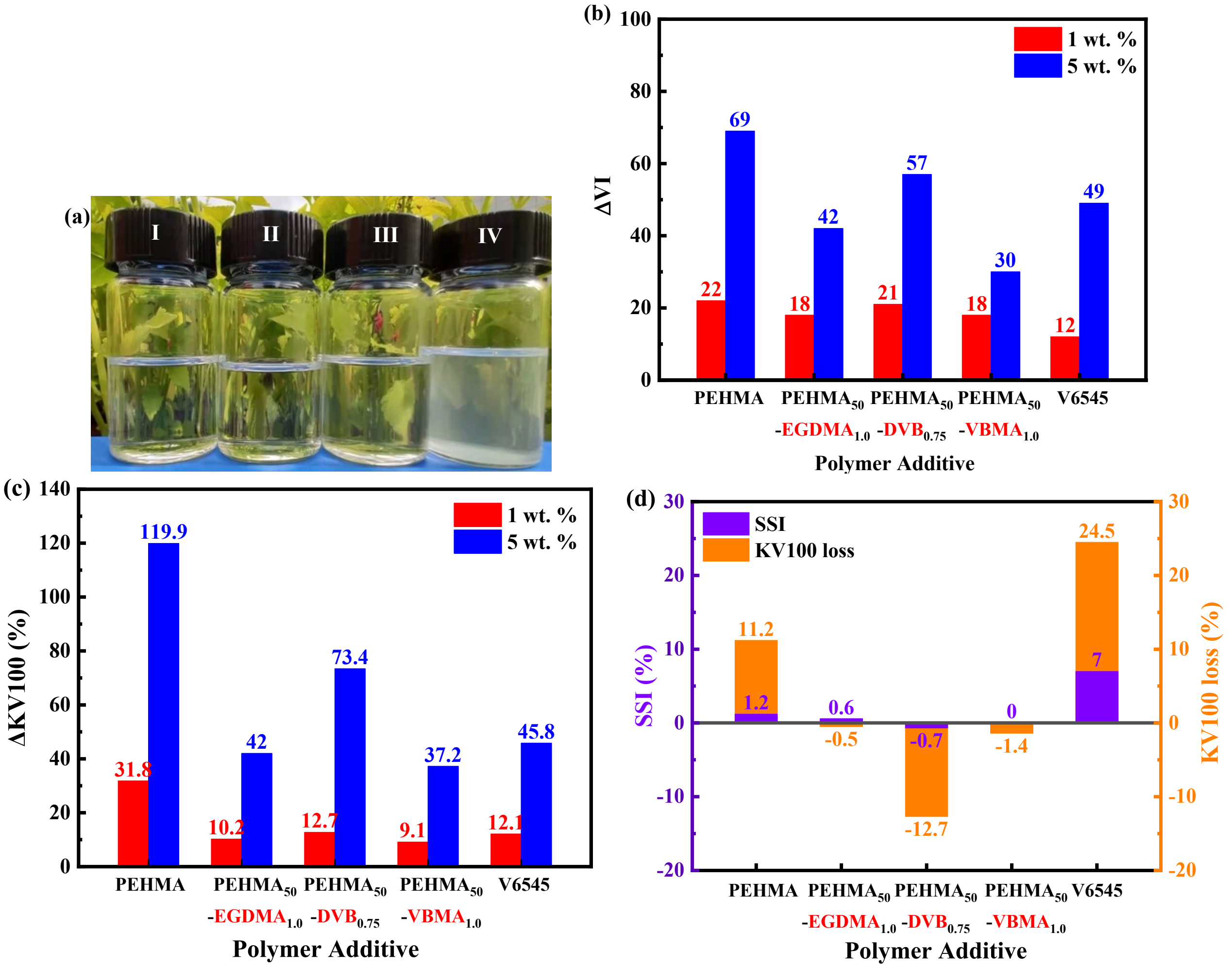

Figure S5. (a) Appearance of $PEHMA_{50}$-$DVB_{0.75}$-formulated lubricants with a concentration of 1 wt% (I) or 5 wt% (II), and $PEHMA_{600}$-formulated lubricants with a concentration of 1 wt% (III) or 5 wt% (IV), as well as (b) ΔVI, (c) ΔKV100 (d) SSI and KV100 loss of lubricants formulated with polymers at different concentrations.

4. References

[1] C. Pugh, V. Percec, *Polym. Bull.*, 1985, **14**, 109-116.

[2] H. F. Gao, A. Miasnikova, K. Matyjaszewski, *Macromolecules*, 2008, **41**, 7843-7849.

[3] Y. Lebigot, M. Delmas, A. Gaset, *Synthetic Commun.*, 1983, **13**, 177-182.