Supporting Information

Conformational, Crystalline and Rheological Properties of Poly(octadecyl-*co*-methyl acrylate) Statistically Random Copolymers

Xuejun Pan,[1,3,†] Weiling Wu,[4,†] Mo Zhu,[1,†] Jixian Yang,[1] Zhi-Chao Yan[2*] and Lianwei Li[1,*]

[1]*College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, China*

[2]*School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China*

[3]*Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China*

[4]*Shenzhen Key Laboratory of Polymer Science and Technology, Guangdong Research Center for Interfacial Engineering of Functional Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518055, China*

[*] To whom corresponding should be addressed:

Zhi-Chao Yan: zcyan@gdut.edu.cn; Lianwei Li: lianweili@szu.edu.cn

Calculation of d*n*/d*c* Values for P(ODA$_x$-*stat*-MA$_y$)$_{N\mathrm{b}}$ copolymers. In this work, we used the classical additive rule to extract (d*n*/d*c*)$_{\mathrm{comb}}$ for P(ODA$_x$-*stat*-MA$_y$)$_{N\mathrm{b}}$ copolymers. Before calculating (d*n*/d*c*)$_{\mathrm{comb}}$, d*n*/d*c* of homopolymer PMA and PODA must be obtained first. First of all, for P*t*BA, the precursor chain of PMA, we already know that its real dn/dc value is 0.052 according to previous work.[1] Therefore, by using QD-SEC, we can know the absolute molar mass of P*t*BA, through which we can calculate the true N_{b} of PMA, thus we can know the true molar mass of the corresponding homopolymer PMA and PODA. Furthermore, we do know that the output value of M_{w} by QD-SEC is inversely proportional to the input value of (d*n*/d*c*)$_{\mathrm{comb}}$ during the analysis process of QD-SEC data, which further leads to

$$M_{\mathrm{LS}} = \Gamma / [(\mathrm{d}n / \mathrm{d}c)_{\mathrm{comb}}] \tag{1}$$

where the pre-factor Γ is a feature parameter and Γ possesses a unique numerical value for a specific sample. More importantly, Γ for each P(ODA$_x$-*stat*-MA$_y$)$_{N\mathrm{b}}$ sample can be easily determined in QD-SEC measurement. By using equation 1, we can characterize PMA and PODA and calculate their d*n*/d*c* as 0.076 and 0.071 respectively, which are very close to the values given in literature and polymer handbook.[2-3] In addition, the expression of copolymer (d*n*/d*c*)$_{\mathrm{comb}}$ value can be expressed as follows:

$$\begin{aligned}(\mathrm{d}n / \mathrm{d}c)_{\mathrm{comb}} &= wt\%_{\mathrm{PMA}} (\mathrm{d}n / \mathrm{d}c)_{\mathrm{PMA}} + wt\%_{\mathrm{PODA}} (\mathrm{d}n / \mathrm{d}c)_{\mathrm{PODA}} \\ &= \frac{M_{\mathrm{MA}}(1-x)}{M_{\mathrm{MA}}(1-x)+M_{\mathrm{ODA}}x}(\mathrm{d}n / \mathrm{d}c)_{\mathrm{PMA}} + \frac{M_{\mathrm{ODA}}x}{M_{\mathrm{MA}}(1-x)+M_{\mathrm{ODA}}x}(\mathrm{d}n / \mathrm{d}c)_{\mathrm{PODA}}\end{aligned} \tag{2}$$

M_{MA}: the molar mass of a monomer unit on backbone, and M_{MA} = 86 g/mol.
M_{ODA}: the molar mass of sidechain (ODA) and M_{ODA} = 324 g/mol.
x: the molar fraction of ODA.
$wt\%_{\mathrm{PMA}}$: the mass percentage of PMA.
$wt\%_{\mathrm{PODA}}$: the mass percentage of PODA.
(d*n*/d*c*)$_{\mathrm{comb}}$: the refractive index increment of P(ODA$_x$-*stat*-MA$_y$)$_{N\mathrm{b}}$ polymers.
(d*n*/d*c*)$_{\mathrm{PMA}}$: the refraction index increment of PMA, and (d*n*/d*c*)$_{\mathrm{PMA}}$ = 0.076 mL/g.
(d*n*/d*c*)$_{\mathrm{PODA}}$: the refraction index increment of PODA, and (d*n*/d*c*)$_{\mathrm{graft}}$ = 0.071 mL/g.

By using equation 2, we can calculate $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{comb}}$ of each sample. And inputting the corresponding $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{comb}}$ value into QD-SEC analysis software, we can get the corresponding absolute parameters of each sample. In addition to the molar mass given by QD-SEC, by using the x calculated by ^{1}H-NMR spectrum analysis, we can also calculate the theoretical molar mass based on ^{1}H-NMR information through the Equation 3:

$$M_{\mathrm{NMR}} = N_{\mathrm{b}}[M_{\mathrm{MA}}(1-x) + M_{\mathrm{ODA}}x] \quad (3)$$

All parameter information is summarized in Table S2-4.

Table S1. Summarized molecular parameters of four P*t*BA precursors determined by QD-SEC.

Sample	$M_{w\text{-}LS}$ /(g/mol)	$M_{p\text{-}LS}$ /(g/mol)	$<M_w/M_n>$	N_b
P*t*BA$_{345}$	4.05×10^4	4.12×10^4	1.08	345
P*t*BA$_{1100}$	1.25×10^5	1.41×10^5	1.13	1100
P*t*BA$_{1740}$	2.17×10^5	2.23×10^5	1.14	1740
PtBA$_{2750}$	3.49×10^3	3.52×10^5	1.23	2750

Table S2. Summarized molecular parameters of P(ODA$_x$-stat-MA$_y$)$_{345}$ polymers by QD-SEC and ^{1}H-NMR.

P(ODA$_x$-stat-MA$_y$)$_{345}$	$M_{p\text{-}NMR}$ /(g/mol)	$M_{p\text{-}LS}$ /(g/mol)	$<M_w/M_n>$	R_η/nm	[η] /(mL/g)
0	2.97×10^4	2.97×10^4	1.06	4.46	21.80
0.29	4.65×10^4	5.31×10^5	1.14	5.68	25.95
0.47	6.14×10^4	6.84×10^4	1.12	6.23	25.60
0.68	7.92×10^4	8.58×10^4	1.12	6.72	24.72
0.87	8.83×10^5	1.01×10^5	1.08	6.97	24.08
0.99	1.11×10^5	1.11×10^5	1.10	7.27	23.45

Table S3. Summarized molecular parameters of P(ODA$_x$-stat-MA$_y$)$_{1100}$ polymers by QD-SEC and ^{1}H-NMR.

P(ODA$_x$-stat-MA$_y$)$_{1100}$	$M_{p\text{-}NMR}$ /(g/mol)	$M_{p\text{-}LS}$ /(g/mol)	$<M_w/M_n>$	R_η/nm	[η] /(mL/g)
0	9.46×10^4	9.07×10^4	1.07	12.07	53.52
0.13	1.29×10^5	1.56×10^5	1.15	11.45	65.93
0.39	1.98×10^5	2.07×10^5	1.08	13.37	64.23
0.45	2.11×10^5	2.42×10^5	1.09	12.73	66.04
0.81	3.07×10^5	3.38×10^5	1.09	14.58	60.64
0.99	3.53×10^5	3.80×10^5	1.08	15.15	58.30

Table S4. Summarized molecular parameters of P(ODA$_x$-stat-MA$_y$)$_{1740}$ polymers by QD-SEC and [1]H-NMR.

P(ODA$_x$-stat-MA$_y$)$_{1740}$	$M_{\text{p-NMR}}$ /(g/mol)	$M_{\text{p-LS}}$ /(g/mol)	<M_w/M_n>	R_η/nm	[η] /(mL/g)
0	1.50×10^5	1.53×10^5	1.11	13.46	68.32
0.23	2.46×10^5	2.39×10^5	1.18	15.13	86.42
0.46	3.41×10^5	3.27×10^5	1.19	16.13	82.91
0.65	4.20×10^5	4.31×10^5	1.16	17.48	79.58
0.86	5.05×10^5	5.00×10^5	1.15	18.36	77.95
0.97	5.53×10^5	5.58×10^5	1.15	18.89	74.87

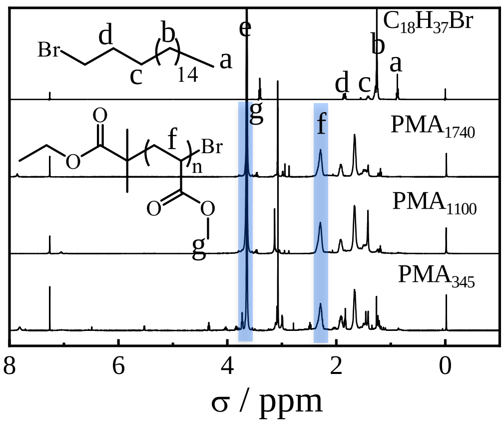

Figure S1. [1]H-NMR spectrum of polymethyl acrylate (PMA) with different backbone length (N_b=345, 1100, 1740) and side chain ($C_{18}H_{37}Br$) in $CDCl_3$.

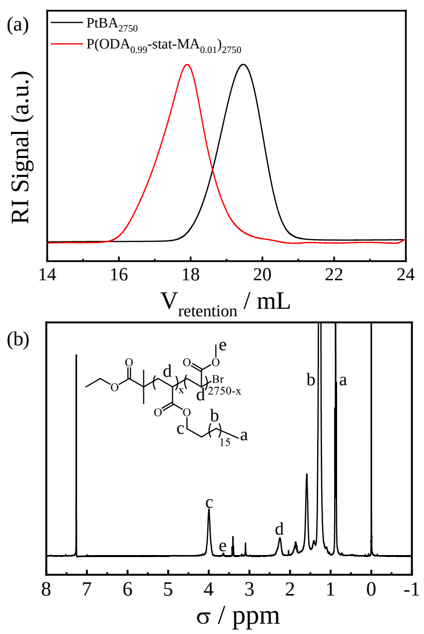

Figure S2. (a) SEC curves of P*t*BA$_{2750}$ and P(ODA$_{0.99}$-stat-MA$_{0.01}$)$_{2750}$ SEC. (b) [1]H-NMR spectra of P(ODA$_{0.99}$-stat-MA$_{0.01}$)$_{2750}$ in $CDCl_3$.

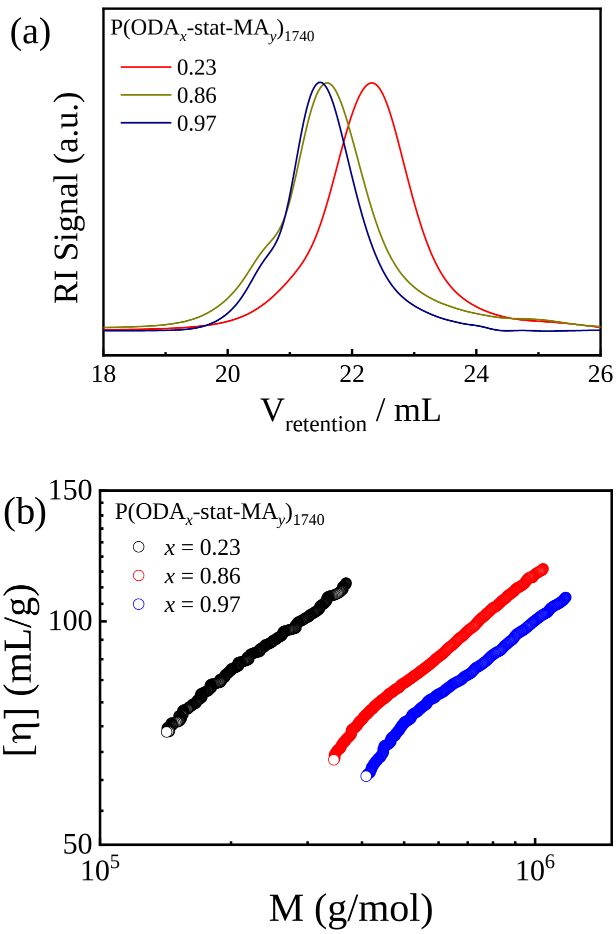

Figure S3. (a) SEC curves of P(ODA$_x$-stat-MA$_y$)$_{1740}$ with three different x (x = 0.23, 0.86, 0.97). (b) Molar mass (M) dependences of intrinsic viscosity ([η]) for P(ODA$_x$-stat-MA$_y$)$_{1740}$ with three different x (x = 0.23, 0.86, 0.97).

In Figures S4a-e, the zero-shear viscosity was obtained by averaging the points in the shear rate independent regime, while the zero-shear viscosity in figure S4f was obtained by the Carreau fitting.[4]

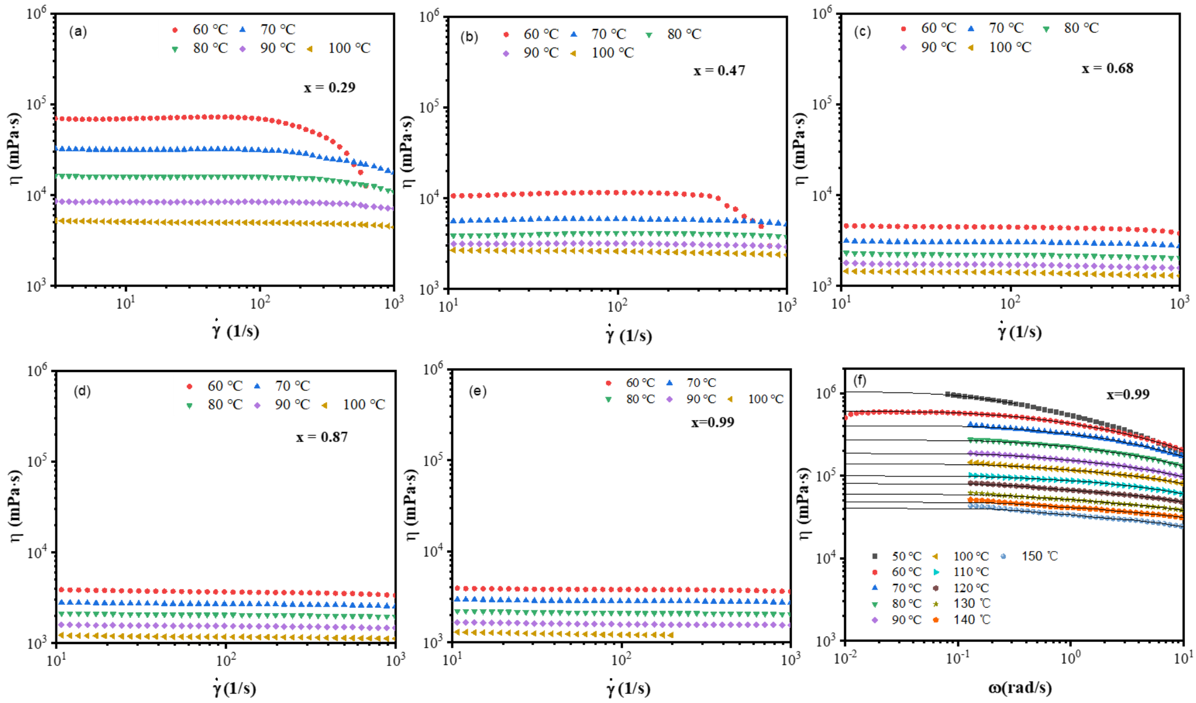

Figure S4. Viscosity (η) as a function of shear rate ($\dot{\gamma}$) for samples with (a) P(ODA$_{0.29}$-stat-MA$_{0.71}$)$_{345}$, (b) P(ODA$_{0.47}$-stat-MA$_{0.53}$)$_{345}$, (c) P(ODA$_{0.68}$-stat-MA$_{0.32}$)$_{345}$, (d) P(ODA$_{0.87}$-stat-MA$_{0.13}$)$_{345}$, (e) P(ODA$_{0.99}$-stat-MA$_{0.01}$)$_{345}$ and (f) Viscosity (η) as a function of frequency (ω) for sample of P(ODA$_{0.99}$-stat-MA$_{0.013}$)$_{2750}$.

References

1. Pan, X.; Ishaq, M. W.; Umair, A.; Ali, M. W.; Li, L., Evolution of Single Chain Conformation for Model Comb-Like Chains with Grafting Density Ranging from 0 to similar to 100% in Dilute Solution. *ACS Macro Letters* **2019**, *8* (12), 1535-1540.
2. Jordan Jr, E. F., Heterogeneity Parameters by Light Scattering for Statistical Copolymers Incorporating Long Side-chain Comonomers. *J Polym Sci Pol Chem* **1968**, *6* (8), 2209-2219.
3. Brandrup, J.; Immergut, E. H.; Grulke, E. A.; Abe, A.; Bloch, D. R., (Eds.), Polymer Handbook. *Wiley: New York*, **1999**.
4. Macosko, C. W.; Larson, R. G., Rheology: Principles, Measurements, and Applications. *Wiley: New York*, **1994**.