Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Rheological Behavior and Molecular Relaxation of Polycations with Macrocounterions in Aqueous Solutions

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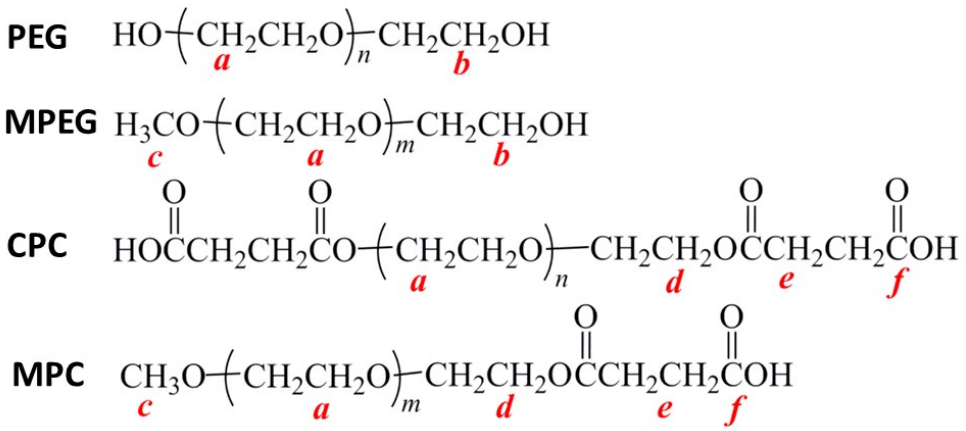
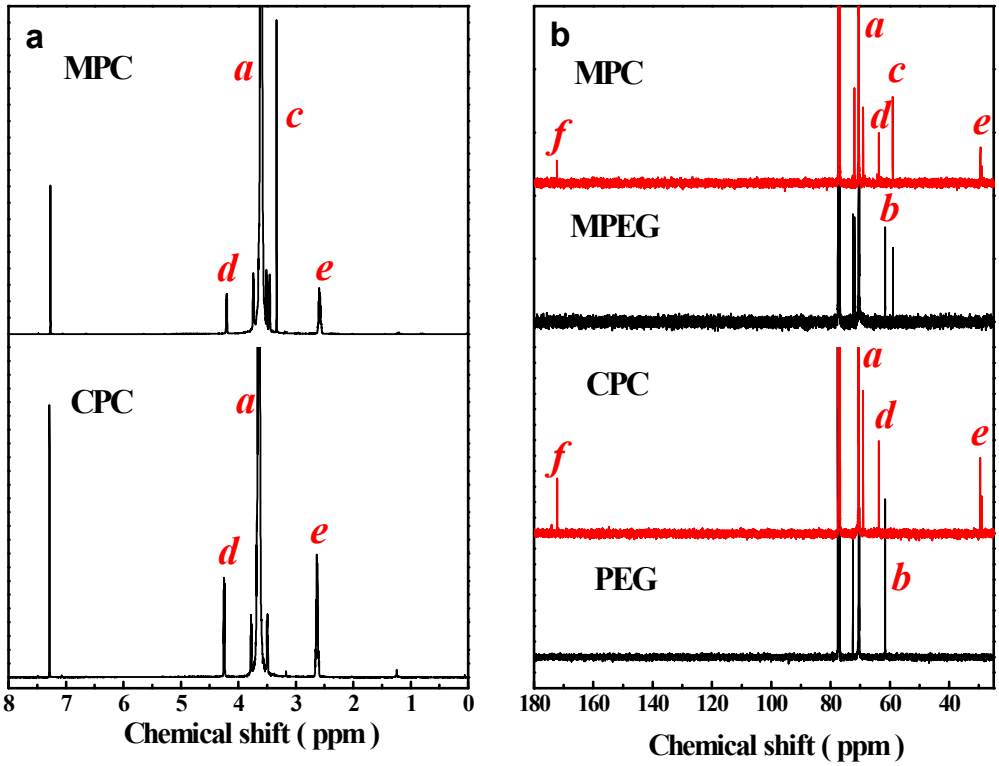


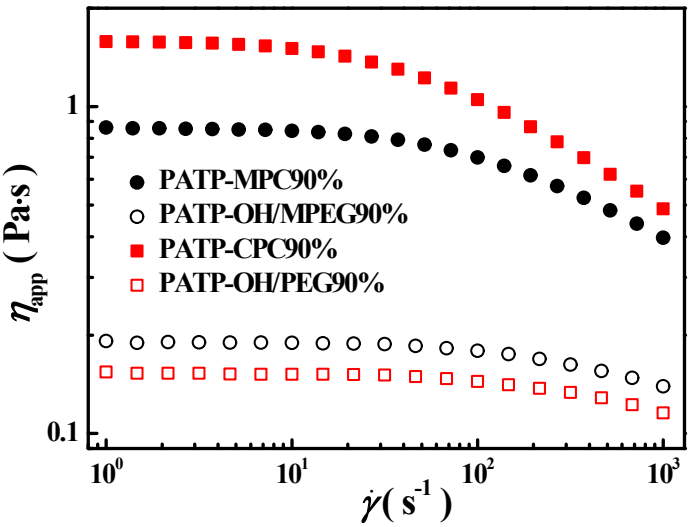
SI. 1 Chemical structures of PEG, MPEG, CPC and MPC.



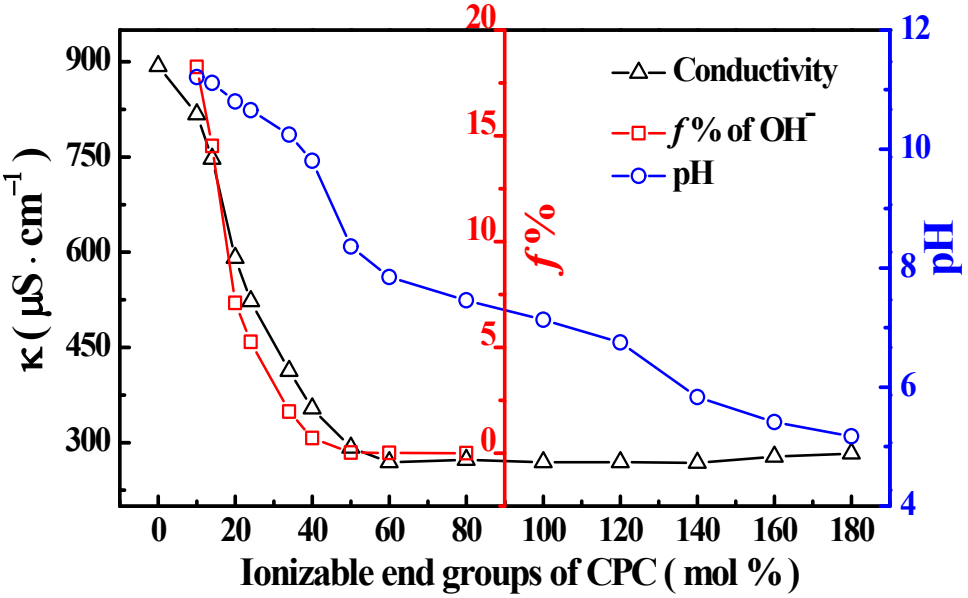
SI. 2 (a) ^{1}H NMR spectra of MPC and CPC and (b) ^{13}C NMR spectra of MPC, MPEG, CPC and PEG using $CDCl_3$ as the solvent.

SI. 1 shows the chemical structures of PEG, MPEG, CPC and MPC and SI. 2 shows (a) ^{1}H NMR spectra of MPC and CPC, and (b) ^{13}C NMR spectra of MPC, MPEG, CPC and PEG. The characteristic peaks in the spectra and their chemical structures are marked by the same red letter. In SI. 2(a), peak *a* at 3.60 ppm is assigned to the backbone of polyethylene glycol (-OCH_2CH_2O-) and peak *c* at 3.33 ppm is assigned to end group CH_3O- of MPC. Peak *d* at 4.20 ppm and peak *e* at 2.59 ppm correspond to -$COOCH_2$- and -$OOCCH_2CH_2COO$- at the modified end groups. The area of peak *c*, *d*, *e* of MPC conforms the ratio 3.0: 2.1: 3.9, which demonstrates complete conversion of end groups of MPC. In SI. 1(b), compared with spectra of PEG and MPEG, MPC and CPC present peak *d*, *e* at 63.7, 29.5 ppm and peak *f* at 172.2 ppm which is assigned to -COOH. Moreover, peak *b* at 61.6 ppm which

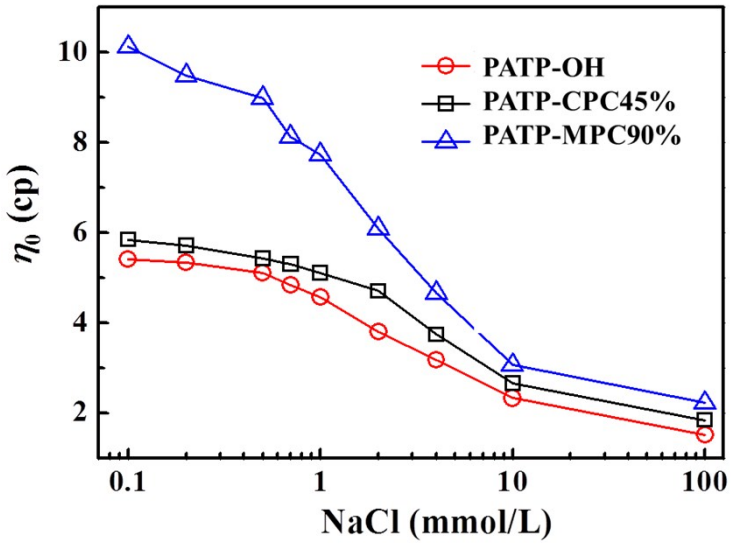
corresponds to the original end group -OH disappears in the spectra of CPC and MPC, which proves complete modification of the end group.



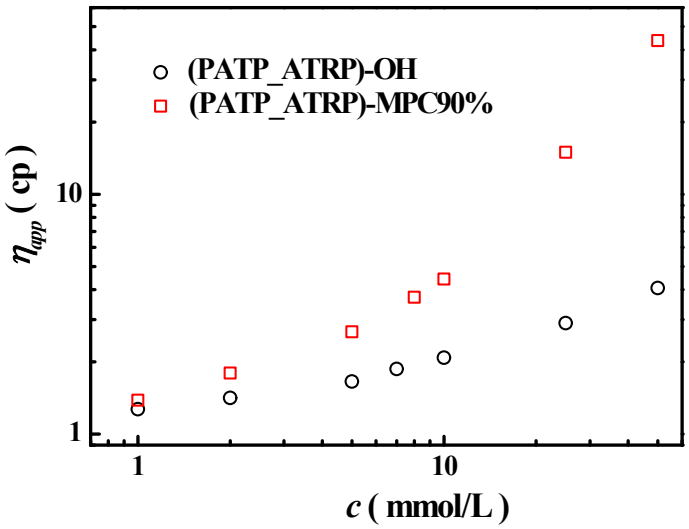
SI. 3 Shear rate dependence of apparent viscosity for sample PATP-MPAC90%, PATP-OH/MPEG90%, PATP-CPC90% and PATP-OH/PEG90%.



SI. 4 Dependence of conductivity (κ), molar fraction of free OH^- (f %) and pH on stoichiometric molar fraction of carboxylate ions of CPC for aqueous solution of PATP-CPC at 9 mmol/L.



SI. 5 Dependence of η_0 on the concentration of NaCl for sample PATP-OH, PATP-CPC45% and PATP-MPC90% at 10 mmol/L.



SI. 6 Dependence of apparent viscosity η_{app} on concentration for (PATP_ATRP)-OH and (PATP_ATRP)-MPC90% synthesized via atom transfer radical polymerization.