Radical Addition-Coupling Polymerization (RACP) towards Sequence-Regulated Copolymer

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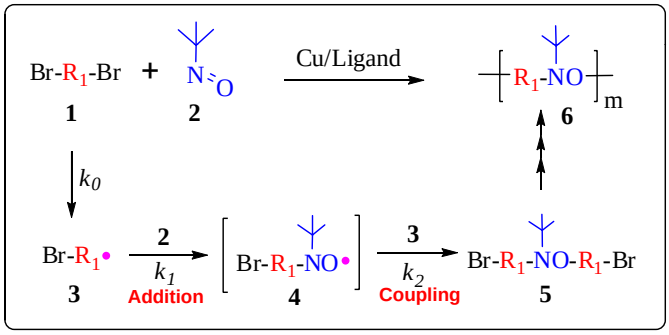
Background

Natural macromolecules, such as proteins and nucleic acids, have various properties originating from their perfectly sequence-regulated chain structures. However, the sequence regulation of synthetic polymers is still beyond the current state of the art in polymer synthesis. Therefore, sequence regulation is one of the most challenging objectives in contemporary polymerization science.

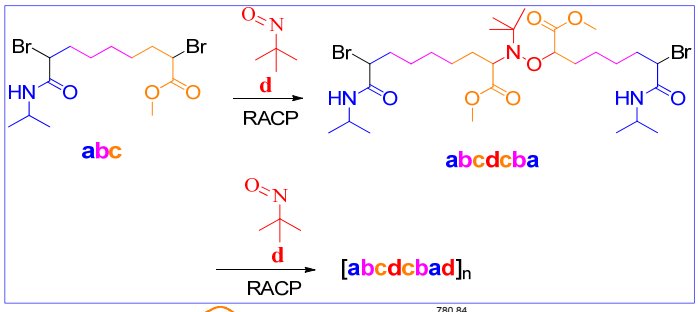
Generally, radical coupling reaction is scarcely used in polymerization although it is a rapid reaction, because radical still undergo disproportionation and transfer reactions by themselves, which makes it impossible to produce polymer with high molecular weight. We report a new type of step-growth radical addition-coupling polymerization (RACP) involving consecutive addition of carbon-centered radical derived from α,α'-dibromo compound to N=O double bond of C-nitroso compound followed by cross-coupling of carbon-centered radical and in-situ formed nitroxyl radical, which produces sequence-regulated copolymers with high molecular weight and unimodal molecular weight distribution from saturated and unsaturated monomers.

Radical Addition-Coupling Polymerization



➢In-situ formation of nitroxyl radical (**4**) via addition of carbon-centered radical generated by redox reaction between α,α'-dibromo compounds and Cu/ligand to N=O double bond of C-nitroso compound followed by cross-coupling of carbon-centered radical (**3**) and nitroxyl radical (**4**) produces alternating copolymers. The so called radical addition-coupling polymerization (RACP) can be applied to synthesize periodic copolymer with alternative monomer sequence from saturated and unsaturated monomer.

RACP of abc-type monomer



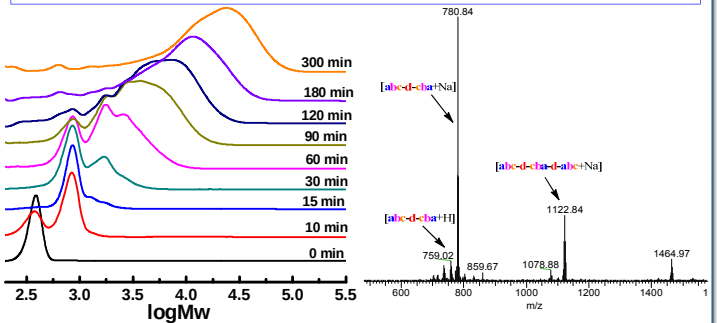
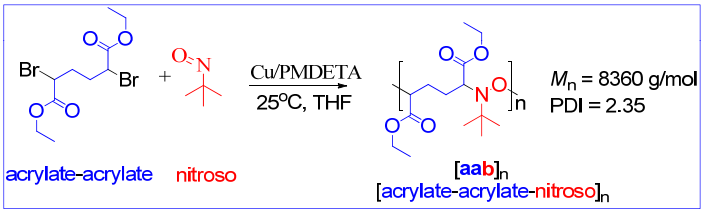
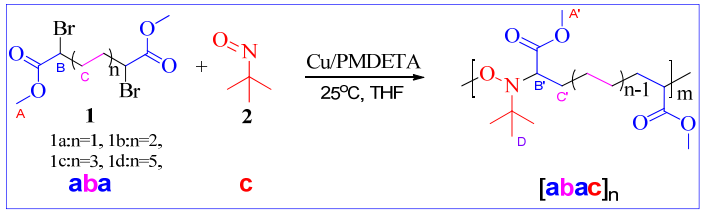


Figure 2. variation of GPC curves of polymers prepared by RACP of abc-type monomer and MNP promoted by Cu/PMDETA (a) and the ESI-MS spectrum of oligomer 2 (10 min) (b) ([abc]:[MNP]:[Cu]:[PMDETA] =1:1:2.2:2, THF=1mL, 25 °C).

RACP of aa-type monomer



RACP of aba-type monomer



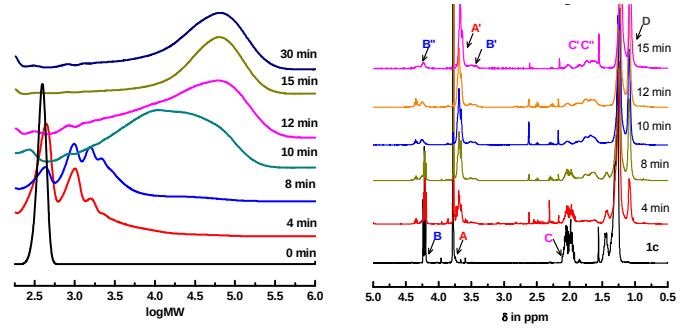


Figure 1. GPC curves and ^{1}H NMR spectra of polymers prepared by step-growth RACP of aba-type monomer and MNP promoted by Cu/PMDETA. $[1d]_0$:$[2]_0$:$[Cu]_0$:$[PMDETA]_0$=1:1:2.2:2, $[2]_0$=0.5M, THF=1mL, 25°C

Conclusion

➢ Reported a new type of radical addition-coupling polymerization (RACP) which could be used to synthesize sequence-regulated copolymer.

➢ Different sequence copolymer could be achieved by RACP of different dibromo compound and unsaturated monomers.

Acknowledgment

➢ Financial support from National Natural Science Foundation of China (21174123) is appreciated.