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Complex polymer architectures via RAFT polymerization: From fundamental process to extending the scope using click chemistry and nature's building blocks

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ABSTRACT

Reversible addition fragmentation chain transfer (RAFT) polymerization has made a huge impact in macromolecular design. The first block copolymers were described early on, followed by star polymers and then graft polymers. In the last five years, the types of architectures available have become more and more complex. Star and graft polymers now have block structures within their branches, or a range of different branches can be found growing from one core or backbone. Even the synthesis of hyperbranched polymers can be positively influenced by RAFT polymerization, allowing end group control or control over the branching density. The creative combination of RAFT polymerization with other polymerization techniques, such as ATRP or ring-opening polymerization, has extended the array of available architectures. In addition, dendrimers were incorporated either as star core or endfunctionalities. A range of synthetic chemistry pathways have been utilized and combined with polymer chemistry, pathways such as 'click chemistry'. These combinations have allowed the creation of novel structures. RAFT processes have been combined with natural polymers and other naturally occurring building blocks, including carbohydrates, polysaccharides, cyclodextrins, proteins and peptides. The result from the intertwining of natural and synthetic materials has resulted in the formation of hybrid biopolymers. Following these developments over the last few years, it is remarkable to see that RAFT polymerization has grown from a lab curiosity to a polymerization tool that is now been used with confidence in material design. Most of the described synthetic procedures in the literature in recent years, which incorporate RAFT polymerization, have been undertaken in order to design advanced materials.

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Abbreviations: 2VP, 2-vinylpyridine; AA, acrylic acid; AAGP, acrylamido glucopyranose; AAm, acrylamide; AcOSty, *p*-acetoxystyrene; AGA, acryloyl glucosamine; AIG, 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose; AN, acrylonitrile; APMA, 2-aminopropyl methacrylamide hydrochloride; AzA, aziodopropylacrylamide; BA, *n*-butyl acrylate; BFA, 2-(*N*-butyl perfluorooctanefluorosulfonamido)ethyl acrylate; BIS, methylene bisacrylamide; BIS–TRIS, *bis*(2-hydroxyethyl)amino–*tris*(hydroxymethyl)methane; BMA, *n*-butyl methacrylate; BzMA, benzyl methacrylate; DEA, *N*,*N*-diethylacrylamide; DEAEMA, 2-(diethylamino) ethyl methacrylate; DIPAMA, *N*,*N*-(diisopropylamino)ethyl methacrylate; DMA, *N*,*N*-dimethyl acrylamide; DMAEA, 2-(dimethylamino)ethyl acrylate; DMAEMA, 2-(dimethylamino)ethyl methacrylate; DMAPMA, 2-(dimethylamino)propyl methacrylate; DTT, dithiothritol; EA, ethyl acrylate; EGDMA, ethylene glycol dimethacrylate; FDA, 1,1,2,2-tetrahydroperfluorodecyl acrylate; FPMA, pentafluorophenyl methacrylate; GMA, glycidyl methacrylate; HEA, 2-hydroxyethyl acrylate; HEMA, 2-hydroxyethyl methacrylate; HPA, 2-hydroxypropyl acrylamide; HPMA, 2-hydroxypropyl methacrylamide; iBor, isobornyl acrylate; IP, isoprene; LA, D,L-lactide; LBAM, 2-lactobionamidoethyl methacrylamide; MA, methyl acrylate; MAA, methacrylic acid; MAGO, 6-*O*-methacryloyl-α-D-glucoside; MAGP, methacrylamido glucopyranose; MAn, maleic anhydride; MIGC11, 3′-(1′,2′:5′,6′-di-*O*-isopropylidene-α-D-glucofuranosyl)-11-methacrylamido undecanoate; MIGC5, 3′-(1′,2′:5′,6′-di-*O*-isopropylidene-α-D-glucofuranosyl)-

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Contents

1. Complex polymer architectures

The interest in polymer architectures beyond undefined linear and branched structures, stems from the unique material properties that can be generated using block copolymers, star polymers, comb polymers and many other unusual polymer architectures such as: palm-tree AB_n, H-shaped B_2AB_2, dumb-bell (pom-pom), ring diblock, star-block $(AB)_n$, amongst many other designs (Fig. 1).

These novel properties arise from the ability of complex architectures to show significantly different solution behaviors as well as from their ability to self-assemble

6-methacrylamido hexanoate; MIGP, 3-*O*-methacryloyl-1,2:3,4-di-*O*-isopropylidene-D-galactopyranose; MMA, methyl methacrylate; NAM, *N*-acryloyl morpholine; NAP, *N*-acryloyl pyrrolidone; NAS, *N*-acryloxysuccinimide; NEMA, *N*,*N*-ethylmethylacrylamide; NIPAAm, *N*-isopropyl arylamide; NNPA, *N*,*N*-propylacrylamide; NVC, *N*-vinylcarbazole; NVP, *N*-vinyl pyrrolidone; P(L-Phe-OMe), poly(*N*-acryloyl-L-phenylalanine methyl ester); PAcOSty, poly(*p*-acetoxystyrene); PAGP, poly(6-*O*-acryloyl-*R*-D-galactopyranose); PBEVB, poly(1-but-3-enyl-4-vinylbenzene); PCL, poly(ε-caprolactone); PDEA, poly(*N*,*N*-diethyl acrylamide); PDMA, poly(*N*,*N*-dimethyl acrylamide); PDMAEMA, poly(2-(dimethylamino)ethyl methacrylate); PDMS, poly(dimethylsiloxane); PEG, poly(ethylene glycol); PEGA, poly(ethylene glycol)acrylate; PEGMA, poly(ethylene glycol) methacrylate; PFPA, pentafluorophenyl acrylate; PHEA, poly(2-hydroxy acrylate); PiBor, poly(isobornyl acrylate); PLA, poly(D,L-lactide); PMA, poly(methyl acrylate); PMMA, poly(methyl methacrylate); PNIPAAm, poly(*N*-isopropyl acrylamide); PNVC, poly(*N*-vinyl carbazole); PNVP, poly(*N*-vinyl pyrrolidone); PPEGA, poly(poly ethyleneglycol acrylate); PS, poly(styrene); P*t*BBPMA, poly(tert-butyl 2-((2-bromopropanoyloxy)methyl)acrylate); PVAc, poly(vinyl acetate); PVAG, poly(6-*O*-vinyladipoyl-D-glucopyranose); PVBC, poly(vinylbenzyl chloride); PVND, poly(vinyl dodecanoate); PVP, poly(*N*-vinyl pyrrolidone); PVPi, poly(vinyl pivalate); SMDB, *N*-(3-sulfopropyl)-*N*-methacrylooxyethyl-*N*,*N*-dimethylammonium betaine; STY, styrene; *t*-BA, tert-butyl acrylate; *t*-BAm, *N*-tert-butyl acrylamide; *t*-BMA, tert-butyl methacrylate; TFT, α,α,α-trifluoro toluene; TMSPMA, trimethylsilyl propargyl methacrylate; VAc, vinyl acetate; VAG, 6-*O*-vinyladipoyl-D-glucopyranose; VBC, 4-vinylbenzyl chloride; VND, vinyl neodecanoate; VPi, vinyl pivalate; VPr, vinyl propionate; VTEMP, 2′-(4-vinyl-[1,2,3]-triazol-1-yl)ethyl-*O*-α-D-mannopyranoside; ε-CL, ε-caprolactone.