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Update and challenges in organo-mediated polymerization reactions

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ABSTRACT

Organocatalysis has become a very powerful tool for precision macromolecular chemistry, as judged by the number of articles published in this field in the past decade. A variety of small organic molecules, including Brønsted/Lewis bases and acids, based on amines, phosphines or carbenes, but also on bi-component systems, have been employed as a means to catalyze the polymerization of miscellaneous monomers. Not only can organocatalysts

Abbreviations: ACEM, active chain-end mechanism; AcOH, acetic acid; AMD, ambrettolide; AMM, activated monomer mechanism; AROPG, anionic ring-opening graft polymerization; BEMP, 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine; BET, bis(2-hydroxyethyl) terephthalate; bis-MPA, 2,2-bis(hydroxymethyl)propanoic acid; BMD, (3S)-3-{[(benzyloxy) carbonyl]methyl}-1,4-dioxane-2,5-dione; BnOH, benzyl alcohol; BNPH, 1,1′-binaphthyl-2,2′-diyl hydrogen phosphate; BO, 1,2-butylene oxide; BOD, [4,4′-bioxepane]-7,7′-dione; BP, 2-butenoxy-2-oxo-1,3,2-dioxaphospholane; BTMC, 3-benzyloxytrimethylene carbonate; Bu_3P, tributylphosphine; BYP, butynyl phospholane; CoAm, poly(*N*,*N*-dimethylacrylamide-co-acrylamide); *Đ*, dispersity; DBN, 1,5-diazabicyclo[4.3.0]non-5-ene; DBSA, dodecylbenzenesulfonic acid; DBU, 1,5-diazabicyclo[5.4.0]undec-5-ene; DFT, density functional theory; DMAP, 4-(dimethylamino)pyridine; DMC, dimethylcarbonate; dMM-LABz, [*R*,*S*]-4-benzyloxycarbonyl-3,3-dimethyl-2-oxetanone; DMTMC, 3,3-dimethoxytrimethylene carbonate; DP, degree of polymerization; DPP, diphenylphosphate; DTC, 2,2-dimethyltrimethylene carbonate; DXO, 1,5-dioxepan-2-one; EBP, 2-ethylbutyl phospholane; EG, ethylene glycol; EO, ethylene oxide; eq., equivalent; EWG, electron withdrawing group; F-TMC, spiro[fluorene-9,5′-[1,3]-dioxan]-2′-one; GB, globalide; GMA, glycidyl methacrylate; GPE, glycidyl phenyl ether; GTP, group transfer polymerization; HMDI, hexamethylene di-isocyanate; iBP, 2-isobutoxy-2-oxo-1,3,2 dioxaphospholane; IDPA, imidodiphosphoric acid; iPP, 2-isopropoxy-2-oxo-1,3,2-dioxaphospholane; L-lacOCA, *O*-carboxyanhydride of lactic acid; L-manOCA, *O*-carboxyanhydride of L-mandelic acid; LA, lactide; LL, laurolactam; M_6TREN, tris[2-(dimethylamino)ethyl]amine; MAC, 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one; MBL, α-methylene-γ-butyrolactone; MMA, methyl methacrylate; MMBL, γ-methyl-α-methylene-γ-butyrolactone; M_n, number average molar mass; M_p, peak average molar mass; M_η, molar mass determined by viscosity measurement; MP, 2-methyl-2-oxo-1,3,2-dioxaphospholane; MPC, 5-methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one; MSA, methane sulfonic acid; MTBD, *N*-methyl-1,5,7-triazabicyclododecene; MTC-Et, 5-methyl-5-ethyloxycarbonyl-1,3-dioxane-2-one; MTS, 1-methoxy-2-methyl-1-[(trimethylsilyl)oxy]prop-1-ene; M_w, weight average molar mass; NCA, *N*-carboxyanhydride; Nf_2NH, bis(nonafluorobutanesulfonyl)imide; NfOH, nonafluorosulfonic acid; NHC-CO_2, azolium-2-carboxylate; NHC-COS, azolium-2-thiocarboxylate; NHC-CS_2, azolium-2-dithiocarboxylate; NHC, *N*-heterocyclic carbene; [NHC(H)][HCO_3], azolium hydrogen carbonate; OBS, *o*-benzenesulfonimide; OCA, *O*-carboxyanhydride; PfOH, perfluorooctane sulfonic acid; PMDETA, *N*,*N*,-*N*′,*N*″,*N*″-pentamethyl diethylenetriamine; P*t*BA, poly(*tert*-butyl acrylate); PTO, 9-phenyl-2,4,8,10-tetraoxaspiro[5,5]undecan-3-one; PTSA, *p*-toluene sulfonic acid; PyBuOH, 4-pyrenebutanol; r.t., room temperature (23 ± 5 °C); SAA, salicylic acid; SKA, silyl ketene acetal; *t*-BuP_2, 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2λ5,4λ5-catenadi(phosphazene); *t*-BuP_4, *tert*-butylimino-tris{[tris(dimethylamino)phosphoranylidene]amino}phosphorane; *t*-OctP_1, *tert*-octylimino-tris(dimethylamino)phosphorane; TBD, 1,5,7-triazabicyclo[4.4.0]dec-5-ene; *t*BGE, *tert*-butyl glycidyl ether; *t*BuA, *tert*-butyl acrylate; Tf_2NH, bis(trifluoromethanesulfonyl)imide; TFA, trifluoroacetic acid; TfOH, trifluoromethanesulfonic acid; T_g, glass transition temperature; TIPSNTf_2, triisopropylsilyl-bis(trifluoromethane)sulfonimide or triisopropylsilyl triflimide; TIPSOTf, triisopropylsilyl trifluoromethanesulfonate or triisopropylsilyl triflate; TMEDA, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; TMOSC, 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane; TMSNTf_2, trimethylsilyl-bis(trifluoromethane)sulfonimide or trimethylsilyl triflimide; TMSOTf, trimethylsilyl trifluoromethanesulfonate or trimethylsilyl triflate; TOF, turnover frequency; TTMPP, tris(2,4,6-trimethoxyphenyl)phosphine; TU, thiourea; ZROP, zwitterionic ring-opening polymerization; β-BL, β-butyrolactone; β-Me 7CC, methyltetramethylene carbonate; β-MLABe, benzyl β-malolactone; β-PL, beta propiolactone; δ-DL, delta decalactone; δ-VL, delta valerolactone; ε-CL, epsilon caprolactone; ε-CLA, epsilon caprolactame; ω-PDL, omega pentadecalactone.

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be employed to promote the ring-opening polymerization of various heterocyclics (*e.g.* lactones, lactide, cyclic carbonates, epoxides, lactams, cyclocarbosiloxanes), but some of them also allow activating vinylic monomers such as (meth)acrylics, or triggering the step-growth polymerization of monomers such as diisocyanates and diols for polyurethane synthesis. The reduced toxicity of organocatalysts in comparison to their metallic counterparts is also driving their development in some sensitive applications, such as biomedical or microelectronics. Overall, organocatalysts display specific monomer activation modes, thereby providing a unique opportunity to control the polymerization of various functional monomers, under mild conditions. This review article focuses on advances of the past 4 years (>150 publications) in polymerization reactions utilizing small organic molecules either as direct initiators or as true catalysts, with a special emphasis on monomer activation modes, as well as polymerization mechanism aspects.

Contents

1. Introduction

Organocatalysis, *i.e.* the use of small organic molecules to catalyze chemical reactions, has gained increased attention over the past 15 years, with an emphasis on asymmetric variants, allowing a variety of biologically active compounds to be accessed [1]. For a long time, highly stereoselective transformations have been mainly achieved using enzymes and transition metal catalysts. However, organocatalysis has become the third branch of catalysis, providing various advantages, including: (i) environmentally more friendly and inherently lower toxicity of organic small molecules, (ii) higher availability of organic reagents, (iii) lower sensitivity toward oxygen and moisture and (iv) large chiral pool [1].

The scope of organocatalytic systems, and their role in various elementary reactions of molecular chemistry have been discussed in detailed reviews [2–5]. They have also been introduced in macromolecular synthesis, where organic reagents can promote polymerization reactions, either as catalysts or as direct initiators, producing polymeric materials exempted of any metallic residues. Related metal-free polymers are thus expected to be employed in high-value and sensitive domains, such as biomedical and personal beauty care applications, microelectronic devices or food packaging.

Several classes of organic activators (catalysts or initiators), including Brønsted/Lewis acids or bases, and mono- or bicomponent bifunctional catalytic systems have been utilized, not only for step-growth and chain-growth