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Polymer engineering based on reversible covalent chemistry: A promising innovative pathway towards new materials and new functionalities

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ABSTRACT

Reversible covalent polymers are able to change their bond arrangement and structure via reversible reaction triggered by external stimuli including heating, light and pH, while retaining the stability of irreversible covalent polymers in the absence of the stimuli. In recent years, more and more research has been devoted to utilization of reversible covalent bonds in synthesizing new materials, which not

Abbreviations: 4-OH-TEMPO, 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy; AAPBA, *N*-acryloyl-*m*-aminophenyl boronic acid; ABS, acrylonitrile-butadiene-styrene copolymer; AFM, atomic force microscopy; AIBN, 2,2-azodiisobutyronitrile; AOBA, 4-allyloxybenzaldehyde; APBA, 4-aminophenylboronic acid; APS, ammonium persulfate; ARES, advanced rheology expanded systems; ATRP, atom transfer radical polymerization; BADGE, bisphenol A diglycidyl ether; BFDGE, bisphenol F diglycidyl ether; BGPDS, bis(4-glycidyloxyphenyl) disulfide; BMA, butyl methacrylate; BMD, 1,12-bis(maleimido)dodecane; BME, 1,2-bis(maleimido)ethane; BMFDMS, bis(2-methoxyfuran) dimethylsilane; BMH, 1,6-bis(maleimido)hexane; BPO, benzoyl peroxide; BSPBA, 4-(3-butenylsulfonyl) phenylboronic acid; CA, citric acid; CANs, covalent adaptable networks; CBA, 4-carboxybenzaldehyde; CCS, core-cross-linked star polymer; CFRCs, carbon fiber reinforce composites; CLCPs, crosslinked liquid-crystalline polymers; CPBA, 4-carboxyphenylboronic acid; DA, Diels-Alder; DABBF, diarylbibenzofuranone; DART, Diels-Alder reversible thermoset; DATBDS, 1,3-diacetoxy-1,1,3,3-tetrabutyl-distannoxane; DBTDL, dibutyltin dilaurate; DBU, 1,8-diazabicyclo(5.4.0)undec-7-ene; DCDC, double cleavage drilled compression; DCM, dichloromethane; DETA, diethylene triamine; DHPM, *N*-(2,3-dihydroxypropyl) maleimide; DIW, direct-ink-writing; DMA, dynamic mechanical analysis; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulphoxide; DPDS, diphenyldisulfide; DPMBM, *N,N*'-4,4′-diphenylmethane-bismaleimide; DPOBM, *N,N*'-4,4′-diphenyloxide bismaleimide; DTDA, dithiodianiline; DTDB, dithiodibutyric acid; EG, ethylene glycol; ENR, epoxidized natural rubber; EPM, ethylene-propylene rubber; EPM-g-MA, ethylene-propylene rubber grafted with maleic anhydride; ESO, epoxidised soybean oil; ESR, electron spin resonance; FA, furfurylamine; FAol, furfuryl alcohol; FF, furfural; FFF, fused filament fabrication; FGE, furfuryl glycidyl ether; FM, furfuryl mercaptan; FMA, 2-furfuryl methacrylate; FTIR, Fourier transform infrared spectroscopy; GC, gas phase chromatography; HAc, acetic acid; HBA, 4-hydroxybenzaldehyde; HBPU, hyperbranched polyurethane; HDI, hexamethylene diisocyanate; HDPE, high-density polyethylene; HEBFMC, 1,6-hexamethylene-bis(2-furanylmethylcarbamate); ^{1}H NMR, proton nuclear magnetic resonance; HPLC, high performance liquid chromatography; IPDI, isophorone diisocyanate; LDPE, low-density polyethylene; LLDPE, linear low-density polyethylene; LMA, lauryl methacrylate; MAAPBA, 4-methacryloyl-m-aminophenylboronic acid; MA-Cu, copper(II) methacrylate; MDI, diphenylmethane diisocyanate; ME, 2-mercaptoethanol; MHHPA, methylhexahydrophthalic anhydride; MMA, methyl methacrylate; MPDBMI, 1,5-bis(maleimido)-2-methylpentane; NMRP, nitroxide-mediated radical polymerizations; PA, polyacrylate; PB, polybutadiene; PBA, poly(*n*-butyl acrylate); PBAG, poly(1,4-butylene adipate glycol); $PBPSF_2$, furyl-telechelic poly(1,4-butylene succinate-co-1,3-propylene succinate); PBS, poly(butylene succinate); PCL, poly(ε-caprolactone); PCMS, poly(4-vinylbenzyl chloride); PCO, polycyclooctene; PDCP, poly(dichlorophosphazene); PDMS, poly(dimethyl siloxane); PDS, polydisulfide; PEA, poly(ethylene adipate); PEAm, polyetheramine; PEG, poly(ethylene glycol); PEGMA, poly(ethylene glycol) methacrylate; PEO, poly(ethylene oxide); PEO-PPO-PEO, copolymer of PEO and PPO; PETMP, pentaerythritol tetra(3-mercaptopropionate); PFMES, poly(2,5-furandimethylene succinate); PHAEs, poly(hydroxyaminoethers); PHUs, poly(hydroxyurethanes); PI, polyimine; PK, polyketone; PLA, poly(lactic acid); PMDETA, *N,N,N*',*N*'',*N*''-pentamethyldipropylenetriamine; PMMA, poly(methylmethacrylate); POSS, poly(hedral oligomeric silsesquioxane); PPDO, poly(*p*-dioxanone); PPDO-PTMEG, poly(*p*-dioxanone)-poly(tetramethylene oxide); PPG, poly(propylene glycol); PPO, poly(propylene oxide); PR, polyrotaxane; PS, polystyrene; PS-b-PEG, polystyrene-block-poly(ethylene glycol); PSOE, polyspiroorthoester; PSOE-co-PAN, copolymer of PSOE and PAN; PTIL, poly(1,2,3-triazolium ionic liquid); PU, polyurethane; PUU, poly(urea-urethane); PVA, poly(vinyl alcohol); PVC, polyvinyl chloride; PVF, poly(vinyl furfural); PVU, poly(vinylogous urethane); PyPBA, 4-pyridineboronic acid; RAFT, reversible addition-fragmentation chain transfer polymerization; ROMP, ring-opening metathesis polymerization; Ru, catalyst ruthenium complex; SBS, poly(styrene-butadiene-styrene); $scCO_2$, supercritical carbon dioxide; SEM, scanning electron microscope; SLS, selective laser sintering; SMASH, shape memory assisted self-healing; SMPs, shape memory polymers; SMPU, shape-memory polyurethane; SOE, spiroorthoester; TAEA, tri(2-aminoethyl)amine; TBD, triazabicyclodecene; TBP, tri-*n*-butylphosphine; TDS, thiuram disulfide; TEA, triethylamine; TEMED, *N,N,N*',*N*'-tetramethylethylenediamine; TEMPO, 2,2,6,6-tetramethylpiperidine-1-oxy; TFA, trifluoroacetic acid; TFPME, tris[(4-formylphenoxy) methyl]ethane; THF, tetrahydrofuran; TMAS, tetramethylammoniumsilanolate; TMEA, tris(2-maleimidoethyl)amine; TMPCA, 2,2,6,6-tetramethylpiperidinyl carboxamide; TPA, terephthaldehyde; Tri-HDI, tri-functional homopolymer of hexamethylene diisocyanate; TsOH, 4-methylbenzenesulfonic acid; TTC, trithiocarbonate; UV–vis, ultraviolet-visible spectroscopy; VBA, 4-vinylbenzaldehyde; VCR, vulcanized chloroprene rubber; VPB, vulcanized polybutadiene; VPBA, 4-vinylphenylboronic acid; WLF, Williams-Landel-Ferry.

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only overcomes disadvantages of permanent covalent polymers, but also brings in new functionalities. More importantly, a series of novel techniques dedicated to polymerized products with features such as properties regulation, self-healing, reprocessing, solid state recycling, and controllable degradation are developed, heralding the opportunity of upgrading of traditional polymer engineering. Although the exploration of this emerging topic is still in its infancy, the advances so far are encouraging and clearly directed to large scale applications. This review systematically outlines this promising trend, following a bottom-up strategy, taking into account both theoretical and experimental achievements. It mainly consists of four parts, involving design and preparation: (i) the basis of reversible covalent chemistry, (ii) rheology of reversible covalent polymers, (iii) methods of construction of reversible covalent polymers, and (iv) smart, adaptive properties offered by reversible covalent chemistry. The key elements for realizing reorganization of polymers containing reversible covalent bonds are covered. The advantages and weaknesses of representative reaction systems are analyzed, while the challenges and opportunities to engineering application of the equilibrium control based on reversible covalent chemistry for producing end-use polymers are summarized. In this way, the readers may grasp both the overall situation as well as insight into future work.

Contents

1. Introduction

Polymer engineering plays a major role in advancement of polymer products and end-user applications. As a key aspect, polymer processing is responsible for converting polymers into finally finished products with desired structure and properties [1,2]. There are different processing techniques specified for different polymers according to their flow behaviors. For thermoplastics, which can be softened or melted by heating, solidified by cooling and remelted repeatedly because of the linear macromolecules, extru-