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Utility of propenyl groups in free radical polymerization: Effects of steric hindrance on formation and reaction behavior as versatile intermediates

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Abstract

2-Substituted-2-propenyl groups can be introduced as polymer ω-end-groups by a variety of means in free radical polymerization. Addition-fragmentation chain transfer (AFCT) and catalytic chain transfer have been employed to

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Abbreviations: AFCT, addition-fragmentation chain transfer; AIBN, 2,2′-azobisisobutyronitrile; ATRP, atom transfer radical polymerization; CHA, cyclohexyl acrylate; CHA-α-*d*, cyclohexyl α-deuterated acrylate; CHMA, cyclohexyl methacrylate; CCT, catalytic chain transfer; COBF, [bis[μ-[(2,3-butanedione dioximato)(2-)-*O*,*O*′]]tetrafluorodiborato(2-)-*N*,*N*′,*N*″,*N*‴]cobalt; COPLY, addition of adduct radical from 2-substitued-2-propenyl ω-end-group to monomer; DCHI, dicyclohexyl itaconate; DIPI, diisopropyl itaconate; D*n*BI, di-*n*-butyl itaconate; DMI, dimethyl itaconate; EA, ethyl acrylate; EBSA, ethyl α-(benzenesulfonylmethyl)acrylate; EEA, ethyl α-ethylacrylate; EHA, 2-ethylhexyl acrylate; EHMA, 2-ethylhexyl methacrylate; ETS, ethyl α-(toluenesulfonylmethyl)acrylates; ESI-MS, electrospray ionization mass spectrometory; FRAG, β-fragmentation of adduct radical from 2-substituted-2-propenyl ω-end-group; GPC, gel permeation chromatography; HEMA-2, unsaturated dimer of 2-hydroxyethyl methacrylate; MA, methyl acrylate; MAD, methyl acrylate unsaturated dimer or methyl α-(2-carbomethoxyethyl)acrylate; MAIB, methyl 2,2′-azobisiobutyrate; MALDI-TOF MS, matrix assisted laser desorption/ionization time of flight mass spectrometry; MAN, methacrylonitrile; MAT, methyl acrylate unsaturated trimer; MATe, methyl acrylate unsaturated tetramer; MBMA, methyl α-(bromomethyl)acrylate; MCM, macromonomer; MCMA, methyl α-(chloromethyl)acrylate; MCR, mid-chain radical; MEA, methyl α-ethylacrylate; MeSt, α-methylstyrene; MIQP, multipulse initiation in pulsed laser and quenched non stationary polymerization; MMAD, methyl methacrylate unsaturated dimmer; MMA-d_8, perdeuterated methyl methacrylate; MMA-3, unsaturated trimer of methyl methacrylate; MMA-4, unsaturated tetramer of methyl methacrylate; MMA-*n*, unsaturated *n*-mer of methyl methacrylate; M_n(GPC), M_n obtained by GPC; M_n(NMR), M_n calculated from content of ω-end-groups using ^{1}H-NMR; MSD, α-methylstyrene unsaturated dimer; MTEA, methyl α-[2,2,2-tris(carbethoxy) ethyl]acrylate; MTMA, methyl α-[2,2,2-tris(carbomethoxy)ethyl]acrylate; *n*BA, *n*-butyl acrylate; *n*BMA, *n*-butyl methacrylate; NOE, Nuclear Overhauser effect; PLP-GPC, pulsed laser polymerization and gel permeation chromatography; PMA-CO_2Me, poly(methyl acrylate) with 2-carbomethoxy-2-propenyl ω-end-group; PMMA-CO_2Me, poly(methyl methacrylate) with 2-carbomethoxy-2-propenyl ω-end-group; PMMA-Ph, poly(methyl methacrylate) with 2-phenyl-2-propenyl ω-end-group; PRR, propagating radical; PSt-CO_2Me, poly(styrene) with 2-carbomethoxy-2-propenyl ω-end-group; PSt-Ph, poly(styrene) with 2-phenyl-2-propenyl ω-end-group; RAFT, reversible addition-fragmentation chain transfer; RMA, alkyl methacrylate; RMA-*n*, unsaturated *n*-mer of alkyl methacrylate; SHAP, steric hindrance assisted polymerization; SP-PLP, pulsed laser polymerization by single pulse laser; SP-PLP-ESR, single pulse laser polymerization-electron spin resonance; St, Styrene; *t*BA, *tert*-butyl acrylate; TEMPO, 2,2,6,6-tetramethylpiperidinyl-1-oxyl; TMIO, 1,1,3, 3-tetramethyl-1,3-dihydro-1*H*-isoindol-2-yloxyl; VAc, vinyl acetate

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introduce the 2-substituted-2-propenyl groups almost quantitatively under appropriate conditions when bimolecular termination cannot compete effectively with these processes as an end forming event. Unsaturated oligomers (dimers, trimers, tetramers and oligomers of higher degrees of polymerization) of methyl methacrylate and methyl acrylate function as carbon–carbon bond cleavage type AFCT agents and can be used to introduce the propenyl end-group. However, these compounds are not as reactive chain transfer agents as carbon-heteroatom bond cleavage type AFCT agents such as α-(bromomethyl)-, α-(alkylthiomethyl)- and α-(arenesulfonylmethyl)acrylates, which effectively reduce the molecular weight of the polymer formed and introduce the propenyl end-group. Mid-chain radicals formed during polymerization of acrylic esters are structurally similar to the radicals generated by radical addition to the 2-carbalkoxy-2-propenyl end-group. β-Fragmentation of the mid-chain radical can be regarded as the reverse reaction of radical addition to the propenyl end-group. Steric congestion accelerates formation of the propenyl end-group via β-fragmentation of the adduct radical, and suppresses intermolecular reactions of the adduct radicals to a larger extent than addition of the propagating radical to the propenyl end-group. Low molecular weight polymers bearing 2-carbalkoxy-2-propenyl and 2-phenyl-2-propenyl ω-end-groups undergo copolymerization as macromonomers with common vinyl monomers, with the exception of poly(methyl methacrylate)s bearing the propenyl end-groups, which primarily act as AFCT agents. Reactivities and reaction modes of α-(substituted methyl)acrylates and related monomers are also described in relation to the behavior of propenyl groups bound to polymer chains.

Keywords: Chain transfer; Steric effect; Fragmentation; Radical polymerization; Competitive reaction; Macromonomer

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Contents

1. Introduction

Radical polymerization is a typical chain reaction consisting of elementary reactions in which the propagating radicals (PRRs) act as chain carriers. The polymerization rate and the molecular weight of the polymer formed are governed by the relative rates of propagation and end forming reactions. In general, polar and resonance effects on monomer and radical reactivities play important roles. These effects, which arise from the same substituents of the monomer and PRR, lead to semi-quantitative or empirical relationships between the reactivities of monomers and radicals. Conjugative monomers such as styrene (St) are more reactive than non-conjugative monomers such as vinyl acetate (VAc) and form less reactive radicals than non-conjugative monomers. Polar factors affect monomer and radical reactivities in the same direction; electron donating and accepting monomers form electron