Progress in Polymer Science 37 (2012) 1004–1030

Contents lists available at SciVerse ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Interpolymer radical coupling: A toolbox complementary to controlled radical polymerization

Antoine Debuigne[a,*], Marie Hurtgen[a], Christophe Detrembleur[a], Christine Jérôme[a], Christopher Barner-Kowollik[b,**], Thomas Junkers[c,***]

[a] Center for Education and Research on Macromolecules (CERM), Chemistry Department, University of Liege, Bldg B6a, Sart-Tilman, 4000 Liege, Belgium
[b] Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany
[c] Institute for Materials Research (IMO), Polymer Reaction Design Group, Universiteit Hasselt, Agoralaan, Gebouw D, BE-3590 Diepenbeek, Belgium

ARTICLE INFO

Article history:
Received 23 September 2011
Received in revised form 20 January 2012
Accepted 27 January 2012
Available online 4 February 2012

Keywords:
Radical coupling
Radical reactions

ABSTRACT

The current review focuses on the relevance and practical benefit of interpolymer radical coupling methods. The latter are developing rapidly and constitute a perfectly complementary macromolecular engineering toolbox to the controlled radical polymerization techniques (CRP). Indeed, all structures formed by CRP are likely to be prone to radical coupling reactions, which multiply the available synthetic possibilities. Basically, the coupling systems can be divided in two main categories. The first one, including the atom transfer radical coupling (ATRC), silane radical atom abstraction (SRAA) and cobalt-mediated radical coupling (CMRC), relies on the recombination of macroradicals produced from a dormant species. The second one, including atom transfer nitroxide radical coupling (ATNRC), single

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Abbreviations: acac, acetylacetonato; AGET, activator generated by electron transfer; ARGET, activator regenerated by electron transfer; AIBN, azobisisobutyronitrile; AN, acrylonitrile; ATNRC, atom transfer nitroxide radical coupling; ATRC, atom transfer radical coupling; ATRCC, atom transfer radical cross coupling; ATRP, atom transfer radical polymerization; BDE, bond dissociation energy; Boc, *tert*-butyloxycarbonyl; bpy, bipyridine; CGCP, chain growth condensation polymerization; CL, caprolactone; CMRC, cobalt-mediated radical coupling; CMRP, cobalt-mediated radical polymerization; CRP, controlled radical polymerization; C_{SC}, spin capturing constant; C_{tr}, chain transfer constant; CuAAC, copper catalyzed azide alkyne cycloaddition; Cy, 1,4,8,11-tetraazacyclotetradecane; DA, Diels–Alder; DBCP, 1,3-diyl-*bis*(2-chloro-2-phenylacetate); DFT, density functional theory; DMSO, dimethylsulfoxide; dNbpy, 4,4′-di(5-nonyl)-2,2′-bipyridine; DT, degenerative chain transfer polymerization; EPR, electron paramagnetic resonance; ESCP, electron spin capturing polymerization; FDA, food and drug administration; GPEC, gradient polymer elution chromatography; HMTETA, 1,1,4,7,10,10-hexamethyltriethylenetetramine; HPG, hyperbranched polyglycerols; IARC, isoprene assisted radical coupling; iPP, isotactic polypropylene; K, equilibrium constant; k_{tc}, termination rate constant by recombination; k_{td}, termination rate constant by disproportionation; k_{tr}, transfer rate constant; LRP, living radical polymerization; Me_6TREN, tris[2-(dimethylamino)ethylamine]; MeOH, methanol; M_n, number average molar mass; MS, mass spectrometry; MW, molecular weight; M_w/M_n, molar mass distribution; MWD, molecular weight distribution; NIPAM, *N*-isopropyl acrylamide; NMP, nitroxide-mediated radical polymerization; NMR, nuclear magnetic resonance; NMRC, nitrone mediated radical coupling; *N*VCL, *N*-vinylcaprolactam; *N*VP, *N*-vinylpyrrolidone; OMRP, organometallic-mediated radical polymerization; PAA, poly(acrylic acid); PAN, poly(acrylonitrile); PBN, *N*-*tert*-butyl-α-phenylnitrone; PCL, poly(caprolactone); PEO, poly(ethylene oxide); PFBuA, poly(*n*-butyl-α-fluoroacrylate); PI, poly(isoprene); P*i*BoA, poly(isobornyl acrylate); PMA, poly(methyl acrylate); PMDETA, pentamethyldiethylenetriamine; PMMA, poly(methyl methacrylate); P*n*BuA, poly(*n*-butyl acrylate); PNIPAM, poly(*N*-isopropyl acrylamide); P*N*VCL, poly(*N*-vinylcaprolactam); P*N*VP, poly(*N*-vinylpyrrolidone); PPhO, poly(phenylene oxide); PPO, poly(propylene oxide); PPX, poly(*p*-xylylene); PRE, persistent radical effect; PS, poly(styrene); P*t*BuA, poly(*t*-butyl acrylate); PVA, poly(vinyl alcohol); PVAc, poly(vinyl acetate); PVImBr, poly(*N*-vinylimidazolium bromide); RAFT, radical addition-fragmentation chain transfer; RATRP, reverse atom transfer radical polymerization; RITP, reverse iodine transfer polymerization; ROMP, ring-opening metathesis polymerization; ROP, ring-opening polymerization; SEC, size exclusion chromatography; SET, single electron transfer; SETNRC, single electron transfer nitroxide radical coupling; $Sn(EH)_2$, tin(II) ethylhexanoate; $Sn(Oct)_2$, tin(II) octanoate; SRAA, silane radical atom abstraction; Sty, styrene; *t*BA, *tert*-butyl acrylate; *t*BB, *tert*-butylbenzene; *t*BuNO, methyl-2-nitrosopropane; TEMPO, 2,2,6,6-tetramethylpiperidine 1-oxyl; THF, tetrahydrofuran; TMS, trimethylsilyl; tolu, toluene; UPy, ureidopyrimidinone; UV, ultraviolet; VA-086, 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide]; VAc, vinyl acetate; VImBr, *N*-vinylimidazolium bromide; X_c, extent of coupling.

[*] Corresponding author. Tel.: +32 4 3663565; fax: +32 4 3663497.
[**] Corresponding author. Tel.: +49 721 608 45642; fax: +49 721 608 45740.
[***] Corresponding author. Tel.: +32 11 26 8318; fax: +32 11 26 8399.
E-mail addresses: adebuigne@ulg.ac.be (A. Debuigne), christopher.barner-kowollik@kit.edu (C. Barner-Kowollik), thomas.junkers@uhasselt.be (T. Junkers).

0079-6700/$ – see front matter
doi:10.1016/j.progpolymsci.2012.01.003

Controlled/living radical polymerization
Block copolymers
Telechelic polymers
Macrocycles

electron transfer nitroxide radical coupling (SETNRC), enhanced spin capturing polymerization (ESCP) and nitrone/nitroso mediated radical coupling (NMRC), makes use of a radical scavenger in order to promote the conjugation of the polymer chains. More than a compilation of macromolecular engineering achievements, the present review additionally aims to emphasize the particularities, synthetic potential and present limitations of each system.

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1. Introduction

Conventional radical polymerization is one of the most widespread processes for the industrial production of vinyl polymers. The tolerance of radical species toward numerous functional groups in the monomer and toward protic solvents such as water account for the success of this versatile and easy to implement technology. Nevertheless, the occurrence of irreversible bimolecular reactions between propagating radicals along the polymerization precludes the formation of well-defined polymers and complex macromolecular architectures. This severe limitation was overcome by the development of controlled radical polymerization (CRP) [1–14]. The latter involves additives able to temporarily deactivate the radical chains and to drastically decrease the influence of irreversible termination reactions, like combination and disproportionation. All along the process, a large majority of "dormant" chains are in equilibrium with a very small amount of active ones. As a consequence, the synthesis of polymers with predictable molecular weight (MW), narrow molecular weight distribution (MWD) and various topologies, was made possible. Among the efficient and exhaustively reviewed CRP techniques are nitroxide-mediated radical polymerization (NMP) [1–3], atom transfer radical polymerization (ATRP) [4–6], radical addition-fragmentation chain transfer (RAFT) [7,8], degenerative chain transfer polymerization (DT) [9,10] and organometallic-mediated radical polymerization (OMRP) [11–13].

In spite of the admittedly deleterious impact of termination reactions on CRP and therewith also on the control of the polymer structure, new synthetic opportunities arose from the combination of CRP with radical polymer chain coupling reactions. (Fig. 1) The present review focuses on the relevance and practical benefits of this apparently paradoxical association. For example, when applied to polymers formed by CRP, a quantitative radical coupling reaction leads to well-defined macromolecules with a twice higher molecular weight. Although the coupling of a homopolymer appears pointless at first sight, it is not the case anymore if the precursor is functionalized in its α-position. In this case, such a "convergent" strategy constitutes a straightforward route to the preparation of homotelechelic polymers. (Fig. 1) Moreover, the coupling reaction of diblocks or gradient type copolymers should give access to the corresponding symmetrical copolymers. (Fig. 1) Some might argue that such architectures are easily available by a "divergent" (co)polymerization strategy using a difunctional initiator. However, copolymers prepared according to the "convergent" and "divergent"

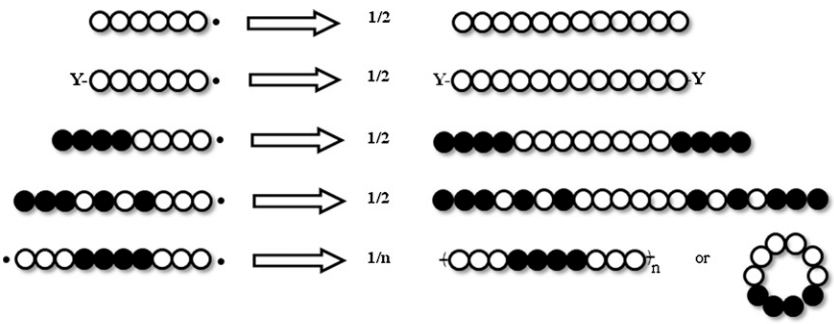

Fig. 1. Schematic representation of synthetic opportunities offered by the radical polymer coupling techniques.