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Stereogradient Polymers by Ruthenium-Catalyzed Stereospecific Living Radical Copolymerization of Two Monomers with Different Stereospecificities and Reactivities

Yu Miura,[†] Takuya Shibata,[†] Kotaro Satoh,[†] Masami Kamigaito,*,[†] and Yoshio Okamoto[‡]

Department of Applied Chemistry, Graduate School of Engineering, and EcoTopia Science Institute, Nagoya University, Nagoya 464-8603, Japan

Received October 27, 2006; E-mail: kamigait@apchem.nagoya-u.ac.jp

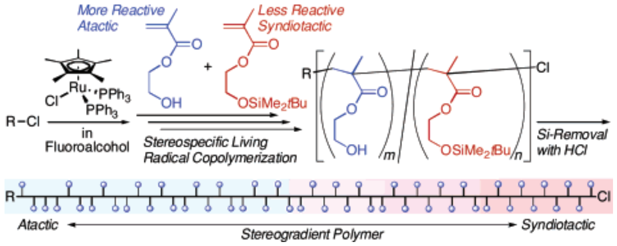
Recently, the development of various living polymerizations has enabled the synthesis of a wide variety of well-defined polymers, including not only end-functionalized, block, graft, and star polymers but also more complex polymers built up by a combination of these architectures.[1] Living radical polymerization is one of the most suitable methods for this purpose in terms of the vast availability of monomers, tolerance to polar functional groups, and easy access to complex architectures.[2] Another recent significant development in precision polymer synthesis has been observed in stereospecific polymerizations, which can drastically alter the thermal and mechanical properties of the resulting polymers depending on the microstructure.[3] Although most of the stereospecific polymerizations were reported for the coordination polymerizations of olefins such as propylene, the stereocontrol during radical polymerizations has recently become possible.[4] Furthermore, a combination of living and stereospecific radical polymerizations permitted not only the simultaneous control of the molecular weight and the tacticity but also the synthesis of stereoblock polymers, in which segments with different tacticities are connected together.[5]

Gradient copolymers are a new class of polymers, in which the instantaneous composition continuously varies along each chain, and were recently prepared by living radical copolymerization.[6] This copolymer has a unique feature different from traditional block and random copolymers due to the continuous change in the composition from one end of the chain to the other and is expected as a new type of functional copolymer, in which the properties gradually change along the main chain.[6,7]

This study is directed toward the synthesis of stereogradient polymers by the stereospecific living radical copolymerization of two monomers that have different stereospecificities and reactivities. Stereogradient polymers can be defined as the polymers in which the tacticity continuously varies along the chain and have never been synthesized except for a few examples.[8,9] Although a quite recent study of the living degenerative-transfer Ziegler−Natta polymerizations revealed the first example of stereogradient poly(propylene),[9] the synthetic methods for stereogradient polymers have not been well established. We now report the first synthesis of stereogradient polymers of 2-hydroxyethyl methacrylate (HEMA), the polymers of which are utilized as functional biocompatible materials,[10] via the ruthenium-catalyzed stereospecific living radical copolymerizations of HEMA[11] and the silyl-capped HEMA [(*tert*-butyldimethylsilyl)-HEMA (SiHEMA)] in a fluoroalcohol (Scheme 1).

Prior to the copolymerizations, preliminary experiments involving the homopolymerizations of each monomer by the ruthenium-based systems [H−(MMA)$_2$−Cl/RuCp*Cl(PPh$_3$)$_2$/*n*-Bu$_3$N] gave the living polymers with controlled molecular weights and narrow molecular weight distributions (MWDs) even in (CF$_3$)$_2$C(Ph)OH at 0 and 60 °C (Supporting Information). However, the tacticity depended on the two monomers; HEMA was polymerized to give less syndiotactic or more or less atactic polymers [$rr = 59.0\%$ (0 °C) and 51.4% (60 °C)],[12] while SiHEMA resulted in syndiotactic-rich polymer [$rr = 77.2\%$ (0 °C) and 66.9% (60 °C)]. This is due to the remarkable solvent effects of such a bulky fluoroalcohol on the radical polymerizations of alkyl methacrylates and HEMA.

Scheme 1. Stereogradient Polymers by Ru-Catalyzed Living Radical Copolymerization of HEMA and SiHEMA



The two monomers were then copolymerized with the ruthenium-based systems in the fluoroalcohol at 0 and 60 °C. The two monomers were consumed at different rates, but simultaneously, in which HEMA was polymerized faster than SiHEMA (Figure 1A). The reactivities obtained from the initial slopes of the first-order plots were about 2.2 times greater for HEMA than for SiHEMA at 0 °C (Figure 1B).

Figure 2 shows the number-average molecular weights (M_n), MWDs, and size-exclusion chromatograms (SEC) of the obtained copolymers. In both cases, the M_n increased in direct proportion to the monomer conversion and agreed well with the calculated values assuming that one molecule of the initiator generates one living polymer chain though the M_n values were based on the PMMA calibration. The SEC curves shifted to high molecular weights with conversion while maintaining narrow MWDs during the polymerizations. Thus, the ruthenium-based system gave the living copolymers from the two monomers in (CF$_3$)$_2$C(Ph)OH.

The copolymers were then converted into poly(HEMA) by the acid hydrolysis of the silyl groups and analyzed by ^{13}C NMR spectroscopy to determine the tacticity of poly(HEMA) (Supporting Information). Figure 3A is a plot of the original SiHEMA ($F_{\mathrm{cum,SiHEMA}}$) contents[6] and the rr (rr_{cum}) of the resulting poly(HEMA) versus the total conversion of the two monomers. These contents are for the cumulative values of the whole chains obtained at each conversion. As the conversions increased, the syndiotacticity was enhanced at both temperatures along with an increase in the original SiHEMA content. This is due to the fact that SiHEMA, which has a lower reactivity than HEMA, shows a higher syndiospecificity at both temperatures. Therefore, a gradual increase in the syndiotacticity was observed with the increasing conversions.

[†] Graduate School of Engineering.
[‡] EcoTopia Science Institute.

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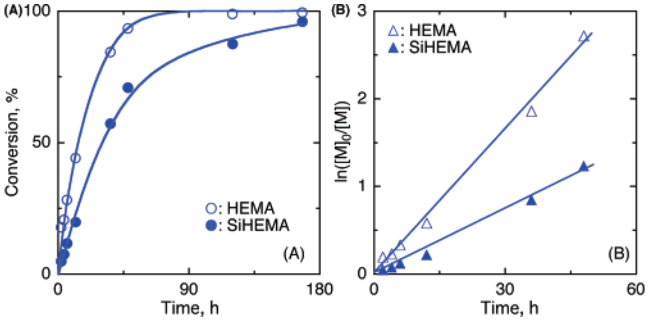

Figure 1. Kinetic plots for the ruthenium-catalyzed copolymerization of HEMA and SiHEMA (0.50/0.50 M) with H$-$(MMA)$_2-$Cl/RuCp*Cl(PPh$_3$)$_2$/*n*-Bu$_3$N (10/4.0/40 mM) in (CF$_3$)$_2$C(Ph)OH at 0 °C.

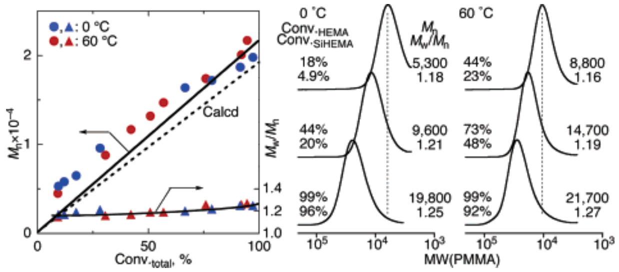

Figure 2. Ruthenium-catalyzed living radical copolymerization of HEMA and SiHEMA (0.50/0.50 M) with H$-$(MMA)$_2-$Cl/RuCp*Cl(PPh$_3$)$_2$/*n*-Bu$_3$N (10/4.0/40 mM) in (CF$_3$)$_2$C(Ph)OH at 0 and 60 °C.

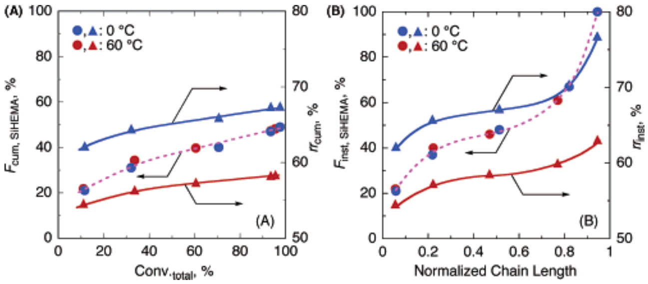

Figure 3. Dependences of SiHEMA and *rr* contents on the total conversion of monomers (A) and the normalized chain length (B) in the ruthenium-catalyzed living radical copolymerization of HEMA and SiHEMA in (CF$_3$)$_2$C(Ph)OH at 0 and 60 °C.

Figure 3B shows the instantaneous composition of SiHEMA ($F_{\text{inst,SiHEMA}}$)[6] and *rr* content (rr_{inst}) plotted versus the normalized chain length of the polymers. Herein, $F_{\text{inst,SiHEMA}}$ and rr_{inst} are for each part that propagates during each sampling interval. The normalized chain length can then be obtained by the total conversion of the monomers, assuming the full chain length as that obtained at the complete conversions. The $F_{\text{inst,SiHEMA}}$ and rr_{inst} were plotted versus the intermediate conversions for each sampling. The rr_{inst} values gradually increased along the normalized chain length similar to $F_{\text{inst,SiHEMA}}$. These sigmoid curves clearly indicate the gradient nature of the two parameters. Especially for the syndiotacticity, the *rr* content gradually increased from 62.2 to 76.8% at 0 °C and from 54.6 to 63.1% at 60 °C. These results indicate the spontaneous formation of the stereogradient polymers by the stereospecific living radical copolymerizations of the two monomers without using a gradual monomer addition technique. Furthermore, linear relationships were observed between rr_{inst} and $F_{\text{inst,SiHEMA}}$, in which the linear plots passed through the *rr* values for the homopolymers (Supporting Information), though the mechanism for the chain growth should be further clarified by investigating the reactivity ratios[6] and cotactic parameters.[13] These stereogradient poly(HEMA) showed the intermediate glass transition temperatures (T_g) for the two homopolymers obtained at the same conditions (Supporting Information). Other properties of the polymers are now under investigation.

In conclusion, this communication revealed a new synthetic method of stereogradient polymers, a new class of polymers, based on the stereospecific living radical copolymerizations of two monomers with different reactivities and stereospecificities. Further expansion of the stereogradient polymers can be expected in terms of the synthetic methods as well as the properties of the new polymers.

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Supporting Information Available: Experimental details and polymerization results. This material is available free of charge via the Internet at http://pubs.acs.org.

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