

Division of Materials Chemistry - Polymer Controlled Synthesis -

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Scope of Research

Our research program focuses on development of new synthetic methods, which enable precise control of polymers in terms of their size and structure. Our attention is especially directed to control of reactive carbon species, such as carbon centered radicals and carbocations, with the aid of synthetic organic chemistry, element chemistry, computational chemistry, and so on. We also study various polymer condensed states by both static and dynamic methods to understand the relation of physical properties and structures.

Research Activities (Year 2007)

Publication

Kayahara E, Yamago S, Kwak Y, Goto A, Fukuda T: Optimization of Organotellurium Transfer Agents for Highly Controlled Living Radical Polymerization, *Macromolecules*, (in press).

Presentations

“Phase Imaging of Polymer Structure by TEM”, Tosaka M, 56th SPSJ Symposium on Macromolecules, Nagoya, Japan, 19–21 September 2007 (invited).

“Effects of Heteroatoms in Highly Controlled Living Radical Polymerizations”, Yamago S, 2007 Japan-Korea Joint Forum on Living/Controlled Polymerization and the Related Subjects, 3 May 2007, Gwanju, Korea (invited).

“Recent Advances in Organoheteroatom-Mediated Living Radical Polymerization”, Yamago S, ICRIS’07, The Science and Technology of Well-Controlled Polymer

Assembly, 11 June 2007, Kyoto (invited).

“Local Structures in Polymer Single Crystals Evidenced by High-Resolution Electron Microscopy”, Tosaka M, Tsuji M, American Chemical Society 234th National Meeting & Exposition, Boston, USA, 19–23 August 2007 (invited).

Grants

Yamago S, Invention of New Radical Chemistry of “Heavy” Group 15 Heteroatom Compounds, Grant-in-Aid for Scientific Research, (A) (2), 1 April 2005–31 March 2008.

Yamago S, Precise Control of Radical Reactions Using Synergetic Effects of “Heavy” Heteroatom Compounds, Grant-in-Aid on Priority Areas, 1 October 2006–31 March 2010.

Yamago S, Precision Control of Organotellurium-

Optimization of Organotellanyl Group Transfer Agents for Highly Controlled Living Radical Polymerization

Living radical polymerization (LRP) has been recognized as one of the most efficient method for the controlled synthesis of macromolecules possessing a variety of polar functional groups with defined monomer sequences and architectures. We have recently developed organotellurium-mediated living radical polymerization (TERP), which shows high versatility in polymerizing varieties of monomer families and gives living polymers with molecular weights predicated from the monomer/transfer agent ratio and with narrow molecular weight distributions. During the course to increase the control over the polymerization, we developed new organotellanyl group transfer agents which gave polymers with lower polydispersity indexes (PDIs); transfer agents possessing aryltellanyl groups, such as phenyltellanyl, *p*-methoxyphenyltellanyl, and *p*-trifluoromethylphenyltellanyl groups, showed higher PDI control than that bearing conventional methyltellanyl group. We also found that *n*-butyltellanyl-substituted transfer agent, which is higher cost efficiency than the conventional agent, exhibited similar control to the conventional one. Kinetic studies revealed that aryltellanyl groups underwent ca. 2–4 times faster tellanyl group transfer reaction than methyltellanyl group towards a polystyrene-end radical, and these results are consistent with the polymerization results.

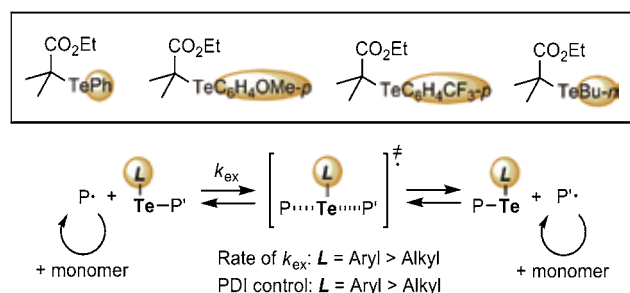


Figure 1. New transfer agents and the key mechanism for the PDI control.

Crystallization of Stretched Network Chains in Crosslinked Natural Rubber

Relatively fast kinetics of strain-induced crystallization (SIC) of crosslinked samples with various network-chain densities (ν) of natural rubber (NR) and its synthetic analogue (IR) was examined by the fast time-resolved wide angle X-ray diffraction and simultaneous tensile measurements. The lateral crystallite size was almost unchanged with elapsed time, though the crystallization proceeded considerably during the period. The rate of SIC was faster for the samples having the higher ν during the first tens of seconds. While the development of SIC obviously depends on ν , progress of relative stress relaxation with time was almost independent of ν . The different dependence of the experimental results on ν was explained by assuming co-existence of stretched and relaxed network chains. During SIC at fixed strain ratio, the intensity of crystalline reflections increased without reducing the intensity of anisotropic amorphous halo on the equator. Accordingly, rather relaxed chains that had shown the off-equatorial scattering were thought to be consumed for the crystal growth.

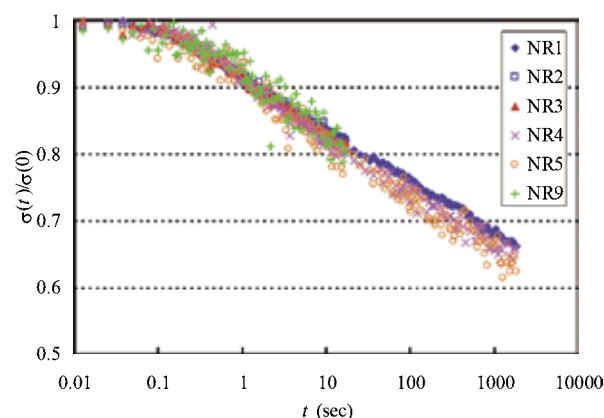


Figure 2. Tensile stress normalized by the maximum stress for NR samples, showing the relative stress relaxation. The smaller number in the sample code corresponds to the higher ν .

Mediated Living Radical Polymerization (TERP), Mitsubishi Foundation Grant, 1 October 2006–30 September 2007.

Yamago S, Creation of Functional Organic Materials by Organobismuthine-Mediated Living Radical Polymerization, Industry-University Joint Research for Innovative Seeds Program, Japan Science and Technology Agency, 1 September 2006–30 September 2007.

Tsuji M, Structure Analysis of Poly(dioxanone) Nanofibers Prepared by Electron-Spinning Method, Grant-in-Aid for Scientific Research, (C), 1 April 2007–31 March 2009.

Tosaka M, Near-Field Optical Effects of Self-Assembled Nanoparticle Chains on Oriented Polymer Layers, The Ogasawara Foundation for the Promotion of Science & Engineering Grant, 1 April 2007–31 March 2008.