Thiol−Ene Modification of 1,2-Polybutadiene Using UV Light or Sunlight

Niels ten Brummelhuis, Christina Diehl, and Helmut Schlaad*

Max Planck Institute of Colloids and Interfaces, Colloid Chemistry, Research Campus Golm, 14424 Potsdam, Germany

Received September 8, 2008
Revised Manuscript Received October 13, 2008

Thiol−ene chemistry, i.e., the free-radical addition of thiols onto double bonds, is a highly efficient tool used for polymerization and curing (vulcanization) reactions and for the modification of polymers.[1,2] The modification route has been applied to various polymers, including rubber,[3] polybutadiene,[4−6] polysiloxane,[7] and polyoxazoline,[8] and to dendrimers.[9] While the modifications of the specialty poly(2-[3-butenyl]-2-oxazoline) and the dendrimer exhibit the characteristics of a "click" reaction,[10] that of the commodity 1,2-polybutadiene (PB) is less efficient because of a seemingly unavoidable side reaction. After the anti-Markovnikov addition of the thiol to the vinyl double bond,[11] the intermediate radical may add, prior to proton transfer, to an adjacent double bond under the formation of a six- or five-member cyclic unit (see Scheme 1).[12] The degree of functionalization may therefore be less than quantitative ($f \sim 0.7-0.8$) at full conversion of double bonds.

The best argument for using 1,2-PB homo- and copolymers is their commercial availability. However, the modification with thiols has been done applying rather harsh and uneconomic conditions (high temperature and large excess of thiol).[5,13] Milder conditions would be desirable, especially when it comes to the synthesis of biohybrid samples containing amino acid, sugar, or cholesteryl entities (see Scheme 1). As will be demonstrated, the thiol−ene modification of 1,2-PB can be performed at low or ambient temperature employing UV light or sunlight for a generation of thiyl radicals (in the absence of photoinitiator) and minimal amounts of solvent. Model reactions have been performed with a 1,2-PB prepared by anionic polymerization ($M_n = 4300$ g/mol, PDI = 1.07, 96% 1,2 units, 56% racemo diads)[14] and methyl 3-mercaptopropionate in tetrahydrofuran (THF) solutions.

The factors affecting the amount of intramolecular cyclization during thiol−ene modification are the concentrations of the components, reaction temperature, and microstructure/tacticity of the PB sample.

The microstructure and tacticity of PB are determined by the synthetic method applied. Samples with a high content of 1,2-units (>90%; residual cis/trans 1,4-units) are produced by anionic[15] or coordination polymerization.[16] The presence of 1,4-units may decrease the probability for intramolecular cyclization. However, in-chain double bonds are 10 times less reactive than vinyl double bonds[7] and may promote an intermolecular cross-linking of chains.[5]

Also, intramolecular cyclization is less favorable when the intermediate radical and the adjacent double bond are located out of plane (racemo) compared to in plane (meso). However, syndiotactic 1,2-PB is a highly crystalline material with poor solubility in common organic solvents (exceptions are chlorinated solvents, which may act as transfer agents in radical reactions).[16] The thiol−ene reaction would then only be possible in dispersion or in bulk (not done) rather than in homogeneous solution. The 1,2-PB produced by anionic polymerization, on the other hand, is not syndiotactic but usually heterotactic (see above).[17]

Since the activation energy of cyclization may be little higher than that of thiyl addition,[18] the cyclization should be repressed upon decreasing the temperature. Also, the thiol−ene addition is a bimolecular reaction whereas cyclization is zeroth order with respect to the concentrations of thiol and double bond. Cyclization should therefore be less favorable the higher is the concentration of reactants (or the less solvent is used).

The following experiments were done using a 2-fold excess of methyl 3-mercaptopropionate (**1**) with respect to 1,2-PB double bonds. Thiyl radicals were directly generated by irradiation with mercury UV lamp (Heraeus TQ 150, 150 W, emphasis of intensity at $\lambda = 303$ nm) in combination with a glass filter.[8] The optically clear (homogeneous) solutions were stirred under an argon atmosphere for 24 h. The products were purified by dialysis and freeze-drying and were analyzed by ^{1}H NMR and elemental analysis (for determination of the conversion of double bonds and the degree of functionalization) and by size exclusion chromatography (SEC) (molecular weight distributions).[5]

The polymers produced by irradiation of mixtures of 1,2-PB and **1** in THF (0.5/2.2/73.4 w/w/w) at temperatures between −35 and +70 °C contained virtually no residual double bonds (<2%). Rather, as expected, the degree of functionalization increased with decreasing reaction temperature, $f = 0.45$ (70 °C), 0.47 (25 °C), and 0.61 (−35 °C). All samples exhibited narrow and monomodal molecular weight distributions.

The concentration series of experiments was done at room temperature. The ratio 1,2-PB/**1** was kept constant (0.5/2.2 w/w), and the amount of solvent was reduced from 73.4 to 0.56 g (corresponding to initial weight fractions of polymer in the mixture of 0.007 to 0.152). The conversion of double bonds was always complete, and the degree of functionalization of the products was found to increase from 0.47 to 0.79 (see Figure 1A). Like before, the products had narrow molecular weight distributions, and there was no evidence for intermolecular cross-linking.

Performing the photoaddition at high concentration (0.5/2.2/0.5 w/w/w) and low temperature (−35 °C) can further improve the efficiency of the reaction, the degree of functionalization reaching a value as high as 0.86.

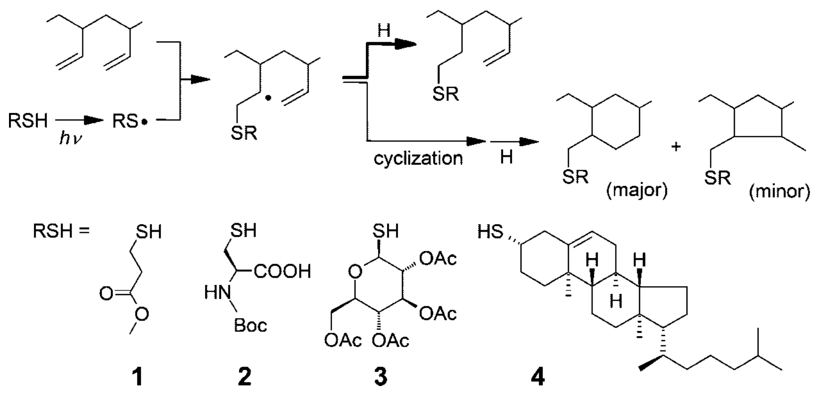
Actually, since the thiol−ene photoreaction can proceed at close to visible wavelengths ($\lambda = 365-405$ nm),[19] it should be possible to generate thiyl radicals using the sun as radiation source. Sealed flasks containing reaction mixtures under an argon atmosphere were placed outside and exposed to sunlight (bright summer day, no clouds) for 18 h without stirring. The conversion of double bonds always came to completion, and the narrow molecular weight distribution of the 1,2-PB precursor was maintained (see Figure 1B). The values of the degree of functionalization were between $f = 0.40$ and 0.79, depending on the composition of the reaction mixture (see Figure 1A).

---

* Corresponding author: fax +49 331 567 9502; e-mail schlaad@mpikg.mpg.de.

10.1021/ma802047w CCC: $40.75

Scheme 1. Pathway of the Radical Photoaddition of Thiols onto 1,2-PB[a]



[a] Structures of thiols: methyl 3-mercaptopropionate (**1**), *N*-Boc-L-cysteine (**2**), 2,3,4,6-tetra-*O*-acetyl-1thio-*β*-D-glucopyranose (**3**), and thiocholesterol (**4**).

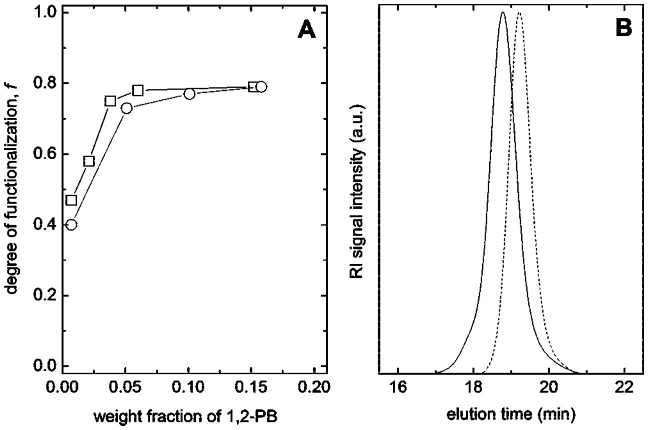


Figure 1. (A) Effect of the concentration of reactants on the efficiency of the photoaddition of methyl 3-mercaptopropionate (**1**) onto 1,2-PB (ratio = constant) at room temperature using UV light (☐) and sunlight (○). (B) SEC trace of the product obtained at the highest concentration in sunlight (solid line) and of the corresponding 1,2-PB precursor (dashed line).

Evidently, the results are similar irrespective of the radiation source (UV or sunlight) used. Kinetic investigations of the thiol−ene reaction are in progress; first results indicate that the half-life of the reaction may be in the order of an hour.

The process was extended to the production of polymers containing biologically active amino acid, sugar, and cholesteryl side chains. Mixtures of 1,2-PB and either **2**, **3**, or **4** in THF (weight fraction of 1,2-PB = 0.023−0.062, [C=C]/[thiol] = 1:2) were exposed to UV light for 24 h (see Supporting Information for details). The degrees of functionalization of the biohybrids were determined to be 0.38, 0.46, and 0.24, respectively, and all samples contained significant amounts of residual double bonds (see the ^{1}H NMR spectra in the Supporting Information). Both findings might be attributed to the steric bulkiness of the thiols. However, higher degrees of functionalization and complete conversion of double bonds might be achieved upon increasing concentrations of reactants and temperature (not done).[5,13,20]

In summary, we described a mild and economical procedure for the thiol−ene modification of 1,2-polybutadiene. Thiyl radicals are generated directly through irradiation with UV light or sunlight. The degrees of functionalization can reach values of ~80% or higher when the photoaddition reaction is performed at high concentrations of reactants ([C=C]/[thiol] = 1:2) and low temperatures. The procedure can be applied for the production of for instance biohybrid polymers containing pendent amino acid, sugar, or cholesteryl entities.

Acknowledgment. Marlies Gräwert, Cliff Janiszewski, Olaf Niemeyer, Sylvia Pirok, and Erich C. (MPI-KG) and Florian Puschmann (ETH Zürich) are thanked for their contributions to this work. Financial support was given by the Max Planck Society.

Supporting Information Available: Descriptions of experimental procedures and of additional experiments as well as NMR (^{1}H, ^{13}C, ^{135}DEPT, and HMQC) and SEC data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hoyle, C. E.; Lee, T. Y.; Roper, T. *J. Polym. Sci, Part A: Polym. Chem.* **2004**, *42*, 5301–5338.
(2) Lutz, J.-F.; Schlaad, H. *Polymer* **2008**, *49*, 817–824.
(3) Serniuk, G. E.; Banes, F. W.; Swaney, M. W. *J. Am. Chem. Soc.* **1948**, *70*, 1804–1808.
(4) Boutevin, B.; Hervaud, Y.; Mouledous, G. *Polym. Bull.* **1998**, *41*, 145–152.
(5) Justynska, J.; Hordyjewicz, Z.; Schlaad, H. *Polymer* **2005**, *46*, 12057–12064.
(6) Ameri David, R. L.; Kornfield, J. A. *Macromolecules* **2008**, *41*, 1151–1161.
(7) Herczynska, L.; Lestel, L.; Boileau, S.; Chojnowski, J.; Polowinski, S. *Eur. Polym. J.* **1999**, *35*, 1115–1122.
(8) Gress, A.; Völkel, A.; Schlaad, H. *Macromolecules* **2007**, *40*, 7928–7933.
(9) Killops, K. L.; Campos, L. M.; Hawker, C. J. *J. Am. Chem. Soc.* **2008**, *130*, 5062–5064.
(10) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.
(11) Griesbaum, K. *Angew. Chem., Int. Ed.* **1970**, *9*, 273–287.
(12) The preferential formation of six- over five-member cycles (Scheme 1) is supported by ^{135}DEPT and HMQC NMR analysis of an ester-modified PB sample; see Supporting Information.
(13) Hordyjewicz-Baran, Z.; You, L.; Smarsly, B.; Sigel, R.; Schlaad, H. *Macromolecules* **2007**, *40*, 3901–3903.
(14) The number-average molecular weight (M_n) and polydispersity index (PDI) were determined by SEC (eluent: THF) based on a calibration with 1,2-PB standards (Polymer Standards Service, Mainz, Germany). NMR spectroscopy (Bruker DPX-400) was applied to determine the microstructure (^{1}H NMR, solvent: $CDCl_3$) and tacticity (^{13}C, solvent: 1,4-dioxane-d_8) (see Supporting Information).
(15) Bywater, S. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989; Vol. *3*, pp 433−447.
(16) Bertini, F.; Canetti, M.; Ricci, G. *J. Appl. Polym. Sci.* **2004**, *92*, 1680–1687.
(17) Mochel, V. D. *J. Polym. Sci., Part A1* **1972**, *10*, 1009–1018.
(18) Denisova, T. G.; Denisov, E. T. *Russ. Chem. Bull.* **2002**, *51*, 949–960.
(19) Jonkheijm, P.; Weinrich, D.; Köhn, M.; Engelkamp, H.; Christianen, P. C. M.; Kuhlmann, J.; Maan, J. C.; Nüsse, D.; Schroeder, H.; Wacker, R.; Breinbauer, R.; Niemeyer, C. M.; Waldmann, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 4421–4424.
(20) You, L.; Schlaad, H. *J. Am. Chem. Soc.* **2006**, *128*, 13336–13337.

MA802047W