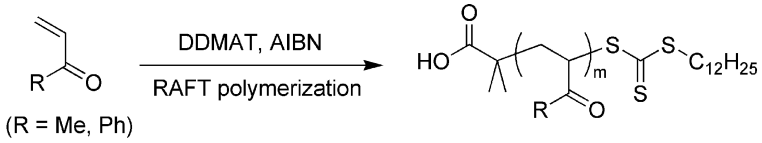
Communication

Well-Defined Vinyl Ketone-Based Polymers by Reversible Addition–Fragmentation Chain Transfer Polymerization

Chong Cheng, Guorong Sun, Ezat Khoshdel, and Karen L. Wooley

J. Am. Chem. Soc., **2007**, 129 (33), 10086-10087• DOI: 10.1021/ja073541y • Publication Date (Web): 28 July 2007



well-defined photodegradable polymers

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Well-Defined Vinyl Ketone-Based Polymers by Reversible Addition−Fragmentation Chain Transfer Polymerization

Chong Cheng,[†] Guorong Sun,[†] Ezat Khoshdel,[‡] and Karen L. Wooley*,[†]
Center for Materials Innovation, Departments of Chemistry and Radiology, Washington University, St. Louis, Missouri 63130-4899, and Unilever Research, Port Sunlight, Quarry Road East, Bebington CH63 3JW, U.K.

Received May 21, 2007; E-mail: klwooley@wustl.edu

As a class of polymers with high photodegradability,[1] vinyl ketone-based polymers have been not only used as "green" materials for packing and agricultural films[2] but also employed as functional materials for imaging, microfabrication, and sensing.[3] Typically, these polymers were synthesized by conventional radical polymerization and, therefore, lacked accurate structural control. Well-defined vinyl ketone-based polymer architectures are required to further extend their applications in the precise syntheses of complex materials, which can be assembled and altered based on structure, composition, and modification, including via photodegradation or other ketone chemistries. Throughout the past decade, living radical polymerization (LRP) has become one of the most powerful synthetic tools for the preparation of well-defined polymers.[4−6] However, as discovered by Mittal et al.,[7] atom transfer radical polymerization (ATRP), an important LRP technique, suffers significant restrictions in polymerizing methyl vinyl ketone (MVK), a representative vinyl ketone monomer, due to unfavorable coordination between the monomer and metal catalyst. Relative to other LRP techniques, RAFT polymerization provides homogeneous and metal-free living polymerization systems applicable for a wide variety of monomers under relatively mild reaction conditions.[6] With interests in defining methods for the syntheses of carbonyl-functionalized polymers and exploring their potential applications,[8] we have studied RAFT polymerization of vinyl ketones and established it as a facile method for the synthesis of well-defined vinyl ketone-based polymers (Scheme 1).

Scheme 1. Well-Defined Vinyl Ketone-Based Polymers by RAFT Polymerization

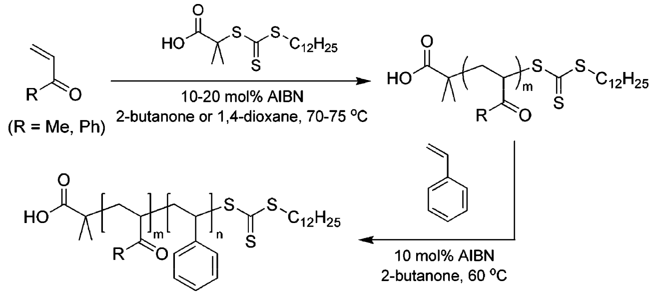


Table 1. RAFT Homopolymerization of Vinyl Ketones[a]

entry	M	$[M]_0$/ $[DDMAT]_0$/ $[AIBN]_0$	T (°C)	t (h)	yield (%)	M_n (kDa) calcd[b]	M_n (kDa) exptl[c]	PDI[d]
1	MVK	100:1:0.2	75	6	80	5.97	7.35 (7.18)	1.19
2	MVK	200:1:0.2	75	4	53	7.79	9.17 (9.37)	1.18
3	MVK	200:1:0.2	75	6	72	10.5	11.4 (11.9)	1.21
4	PVK	100:1:0.1	70	20	40	5.67	5.82	1.16
5	PVK	100:1:0.2	75	6	65	8.98	7.70	1.18

[a] Solvent: 60 vol % 1,4-dioxane for trial 3, 50 vol % 2-butanone for all other trials. [b] $M_n^{calcd} = (MW_M \times \text{yield\%} \times [M]_0/[DDMAT]_0) + MW_{DDMAT}$. [c] M_n^{GPC} (M_n^{NMR}). [d] By GPC.

RAFT homopolymerizations of two typical vinyl ketone monomers, MVK and phenyl vinyl ketone (PVK), were conducted at 70−75 °C in either 2-butanone (50 vol %) or 1,4-dioxane (60 vol %). 2,2′-Azobis(isobutyronitrile) (AIBN) was used as the initiator, and (*S*)-1-dodecyl-(*S*′)-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate[9] (DDMAT) was selected as the RAFT agent ($[M]_0/[DDMAT]_0/[AIBN]_0 = 100-200:1.0:0.1-0.2$), due to its easy synthesis and less unfavorable odor relative to most other RAFT agents. As shown in Table 1, poly(vinyl ketone)s with well-controlled number-average molecular weights (M_n) and low polydispersities ($PDI^{GPC} = 1.16-1.21$) were synthesized. Besides polymers, small molecule side products (mainly dimers of vinyl ketones) were also formed in the reaction systems with considerable yields (>10%).[10] However, the correspondent side reactions did not interfere considerably with the RAFT polymerization process. Because of competing side reactions, monomer conversions consumed by polymerization could not be obtained by ^{1}H NMR analysis based upon decreased resonance intensities of monomer vinyl protons, rather, they were estimated through recovery yields of polymers. The M_n^{GPC} values of poly(vinyl ketone)s, which were detected by gel permeation chromatography (GPC), relative to linear polystyrene (PSt) standards, agreed with the M_n^{calcd} values based on the estimated conversions, within experimental errors. For the resulting PMVKs, their M_n values could also be determined by ^{1}H NMR spectroscopy. Comparison of the integration for the protons along the polymer chain resonating from 0.7 to 2.5 ppm with the characteristic resonance of the methine proton of the terminal monomer unit at 4.98 ppm and the SCH_2 protons from RAFT functionality at 3.36 ppm gave M_n^{NMR} values that were close to the corresponding M_n^{GPC} values, indicating maintenance of the unique chain-end RAFT group. As a note, for the resulting PPVKs, all these resonances from terminal protons overlapped with resonances from other protons, and therefore, their M_n^{NMR} values were not obtained.

To further identify the living characteristic of the RAFT polymerizations of vinyl ketones, the relationships of monomer conversions for polymerizations versus M_n and PDI of the resulting polymers were studied. Selecting MVK as the representative monomer, a series of RAFT polymerizations ($[M]_0/[DDMAT]_0/[AIBN]_0 = 200:1.0:0.2$) were conducted at 75 °C in 50 vol % 2-butanone for 0.5, 1, 1.5, 2, and 3 h. A linear PSt standard (M_n = 1600 kDa, PDI ≤ 1.12; 2.0 wt % relative to MVK) was added to each trial as external reference for accurate determination of the MVK conversion for polymerization by GPC analysis of the polymerization mixture with dn/dc correction. No significant induction period for polymerization was observed. The M_n^{GPC} values agreed with the M_n^{calcd} values and also had excellent linearity agreement with monomer conversions to polymer (Figure 1). A narrow molecular weight distribution ($PDI^{GPC} = 1.14-1.17$) was obtained in each case.

[†] Washington University.
[‡] Unilever Research.

10.1021/ja073541y CCC: $37.00 © 2007 American Chemical Society

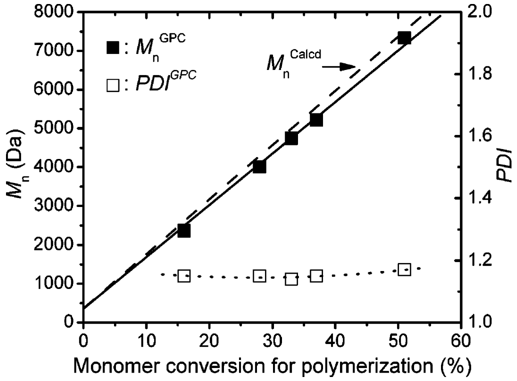


Figure 1. Monomer conversions for polymerization versus M_n^{GPC} and PDI^{GPC} of the resulting polymers for RAFT polymerizations of MVK ($[MVK]_0/[DDMAT]_0/[AIBN]_0 = 200:1.0:0.2$; 50 vol % 2-butanone, 75 °C; polymerization times = 0.5, 1, 1.5, 2, and 3 h).

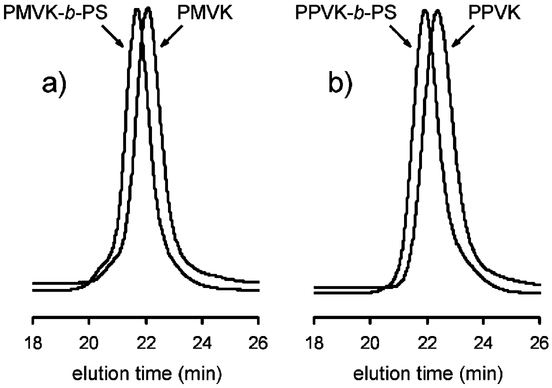


Figure 2. GPC curves of poly(vinyl ketone) homopolymers and block copolymers with polystyrene: (a) PMVK (Table 1, entry 2) and PMVK-*b*-PSt; (b) PPVK (Table 1, entry 5) and PPVK-*b*-PSt (polymerization conditions: $[St]_0/[macro\text{-}RAFT]_0/[AIBN]_0 = 190:1:0.1$; 50 vol % 2-butanone; 60 °C, 12 h; St conversions = ca. 20%).

The living characteristics of RAFT polymerization have allowed ready preparation of a broad variety of block copolymers.[6,8,9,11] Therefore, chain extension from the initial poly(vinyl ketone)s by RAFT polymerization was investigated as a synthetic method for the preparation of photodegradable block copolymers. Using PMVK ($M_n^{GPC} = 9.17$ kDa, $PDI^{GPC} = 1.18$) and PPVK ($M_n^{GPC} = 7.70$ kDa, $PDI^{GPC} = 1.18$) as the macro-RAFT agents and AIBN as the initiator, RAFT polymerizations of styrene ($[St]_0/[macro\text{-}RAFT]_0/[AIBN]_0 = 190:1:0.1$) were conducted at 60 °C in 50 vol % 2-butanone for 12 h. For each trial, ca. 20% conversion of St was reached, as obtained by ^1H NMR analysis of the final polymerization mixtures based upon the resonance intensities of vinyl protons of remaining monomer. As shown in Figure 2, the formation of diblock copolymers PMVK-*b*-PSt ($M_n^{GPC} = 12.3$ kDa, $M_n^{calcd} = 13.2$ kDa; $PDI^{GPC} = 1.18$) and PPVK-*b*-PSt ($M_n^{GPC} = 10.2$ kDa, $M_n^{calcd} = 11.7$ kDa; $PDI^{GPC} = 1.21$) from the chain extension experiments was verified by GPC analyses. The good agreement between the M_n^{GPC} and M_n^{calcd} values of the diblock copolymers and their narrow molecular weight distributions illustrate the quantitative chain transfer efficiency of the poly(vinyl ketone)-based macro-RAFT agents.

As a preliminary application study of these well-defined vinyl ketone-based polymers, polymer films were prepared by drop casting a solution of PMVK-*b*-PSt (2.0 mg/mL) on silicon, followed by annealing at 155 °C for 10 h, UV irradiation (366 nm) for 1 h to degrade PMVK blocks and rinsing with methanol to remove photodegradation products. As demonstrated by tapping mode atomic force microscopy (AFM) measurements, the film has significant nanostructured surface features (Figure 3), which were not possessed by other films without UV irradiation, or methanol rinse, or both (see Supporting Information). Detailed mechanistic studies for the photodegradation[1] are in progress.

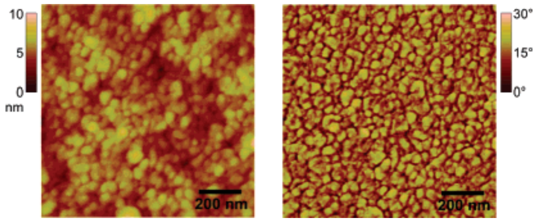


Figure 3. Tapping mode AFM height (left) and phase (right) images of a polymer film prepared from PMVK-*b*-PSt by drop casting a solution on silicon, annealing at 155 °C for 10 h, UV irradiation (366 nm) for 1 h, followed by rinsing with methanol.

In summary, RAFT synthetic strategy has been established as a facile method for the preparation of vinyl ketone-based homopolymers and block copolymers with well-controlled structures. We believe that these polymers can be used for the preparation of hollowed nanostructures with controlled dimensions or cleavable networks through selective assembly and photodegradation.[12] Moreover, via other well-developed ketone chemistries,[13] they may serve as templates for the construction of complex polymeric architectures or conjugates with bioactive agents for biological and medicinal applications.

Acknowledgment. Financial support from Unilever and the National Science Foundation (Grant No. 0451490) is gratefully acknowledged. This material is also based upon work supported by the National Heart Lung and Blood Institute of the National Institutes of Health as a Program of Excellence in Nanotechnology (U01 HL080729).

Supporting Information Available: Experimental Section and AFM images. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Guillet, J. E.; Norrish, R. W. G. *Nature* **1954**, *173*, 625. (b) Wissbrun, K. F. *J. Am. Chem. Soc.* **1959**, *81*, 58. (3) Golemba, F. J.; Guillet, J. E. *Macromolecules* **1972**, *5*, 212.
(2) Guillet, J. E. *Macromol. Symp.* **1997**, *123*, 209.
(3) (a) Sugita, K. *Prog. Org. Coat.* **1997**, *31*, 87. (b) Green, O.; Smith, N. A.; Ellis, A. B.; Burstyn, J. N. *J. Am. Chem. Soc.* **2004**, *126*, 5952.
(4) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661.
(5) (a) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921. (b) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.
(6) (a) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379. (b) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2006**, *59*, 669. (c) Lowe, A. B.; McCormick, C. L. *Prog. Polym. Sci.* **2007**, *32*, 283. (d) Favier, A.; Charreyre, M.-T. *Macromol. Rapid Commun.* **2006**, *27*, 653. (e) Perrier, S.; Takolpuckdee, P. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5347.
(7) Mittal, A.; Sivaram, S.; Baskaran, D. *Macromolecules* **2006**, *39*, 5555.
(8) Sun, G.; Cheng, C.; Wooley, K. L. *Macromolecules* **2007**, *40*, 793.
(9) Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754.
(10) Alder, K.; Offermanns, H.; Ruden, E. *Ber. Dtsch. Chem. Ges.* **1941**, *74B*, 905.
(11) (a) Zhang, L.; Katapodi, K.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2177. (b) O'Reilly, R. K.; Joralemon, M. J.; Hawker, C. J.; Wooley, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5203. (c) Gemici, H.; Legge, T. M.; Whittaker, M.; Monteiro, M. J.; Perrier, S. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2334.
(12) (a) Sanji, T.; Nakatsuka, Y.; Ohnishi, S.; Sakurai, H. *Macromolecules* **2000**, *33*, 8524. (b) Johnson, J. A.; Finn, M. G.; Koberstein, J. T.; Turro, N. J. *Macromolecules* **2007**, *40*, 3589.
(13) (a) Taniguchi, I.; Mayes, A. M.; Chan, E. W. L.; Griffith, L. G. *Macromolecules* **2005**, *38*, 216. (b) Tumelty, D.; Carnevali, M.; Miranda, L. P. *J. Am. Chem. Soc.* **2003**, *125*, 14238. (c) Van Horn, B. A.; Wooley, K. L. *Soft Matter* **2007**, *2*, 1032.

JA073541Y