Macromolecules **2003,** *36,* 6959−6961

Photoinitiated Cross-Linking of Acetylene-Containing Polymers in the Presence of Tungsten Hexacarbonyl

Cristina Badarau and Zhi Yuan Wang*

Department of Chemistry, Carleton University,
1125 Colonel by Drive, Ottawa, Ontario, Canada K1S 5B6

Received May 19, 2003
Revised Manuscript Received August 7, 2003

A wide variety of photo-cross-linkable polymers have been reported during the past 70 years.[1] These polymers possess photoreactive groups in the main chain or side chain that can react upon photoirradiation. Photocycloaddition reactions are applicable to the cross-linking of poly(vinyl cinnamate)s, chalcone-type compounds, bismaleimides, anthracene derivatives, and cyclized polyisoprene. Photochemical [$2\pi + 2\pi$] dimerization is responsible for the cross-linking of poly(vinyl cinnamate)s, while [$4\pi + 4\pi$] dimerization takes place in photo-cross-linking of anthracene-containing polymers.[2] In addition, photoinitiated radical reactions are widely used for curing a variety of vinyl-functionalized polymers.[2]

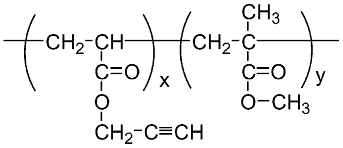
Acetylene moieties have been incorporated into polyimides,[3] poly(aryl ether sulfones),[4] polyphenylenes,[5] polyesters,[6] and poly(phenylquinoxalines)[7] to effect thermal cross-linking. Heating at temperatures above 150 °C induces cross-linking through cyclotrimerization and coupling reactions of the acetylene moieties.[8] However, photoinitiated cross-linking of acetylene-containing polymers has not been reported to date.

Alkyl- and aryl-substituted acetylenes are known to be polymerized by light in the presence of group VI metal carbonyls [e.g., $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$] in halogenated solvents[9a−c] and some other group VI metal complexes.[10] A variety of Lewis acids (e.g., $SiCl_4$ and $GeCl_4$) are effective cocatalysts for polymerization of various acetylenes in nonhalogenated solvents.[11] Among the metal catalysts, tungsten hexacarbonyl, molybdenum hexacarbonyl,[12a] and metal carbonyls of general structure $M(CO)_xL_y$[12b] are widely used for making high molecular weight polyacetylenes.

It is conceivable that, by applying the metal-catalyzed photochemistry of acetylenes to a polymer that contains pendent acetylene groups, one could develop a new photo-cross-linkable polymer system. Such a photocurable system requires the use of only a small amount of $W(CO)_6$ or other effective metal catalysts and is in principle applicable to any polymer that contains the acetylene moiety in the main chain, side chain, or chain ends. We report here the first example of photo-cross-linkable polyacrylates containing acetylene moieties in the side chain in the presence of a small amount of $W(CO)_6$.

A series of acrylate-type polymers **1a**−**1e** having pendent acetylene moieties were synthesized from propargyl acrylate[13] and methyl methacrylate by radical polymerization in benzene (for **1a**−**1d**) or acetone (for **1e**) initiated by benzoyl peroxide.[14] All the polymers were isolated as white powders and displayed excellent solubility in chlorinated hydrocarbons, benzene, *N*,*N*′-dimethylformamide, *N*-methyl-2-pyrolidinone, and *N*,*N*′-dimethylacetamide. Free-standing, tough, flexible, water-transparent films could be cast from the polymer solution in 1,1,2,2-tetrachloroethane (TCE).

Table 1. Characterization of Acetylene-Containing Polymers 1a−1e



1 a-e

polymer	x:y^a	PA (%)^b	M_w^c	M_w/M_n	T_g^d (°C)	T_d^e (°C)
1a	1:32.5	3.0	350 000	1.9	115	285
1b	1:7.6	11.6	375 000	2.4	44	287
1c	1:1.9	34.5	234 000	1.5	51	290
1d	1:0.8	55.5	54 000	1.2	37	325
1e	1:0	100	88 000	8.3	51	335

[a] Molar ratio in the final polymer, as determined from the NMR data. [b] Mol % of propargyl acrylate (PA) in copolymers. [c] By GPC using polystyrene standards. [d] Taken from the second scans of DSC at a heating rate of 10 °C/min. [e] Onset temperature for 5% weight loss in nitrogen, as assessed by TG at a heating rate of 10 °C/min.

The IR bands for the acetylene groups were found at 3300 cm^{-1} (≡C−H) and 2132 cm^{-1} (C≡C), while the ester carbonyl peaks were observed at 1736 cm^{-1}. The ≡C−H peaks in the ^1H NMR spectra were observed at 2.5 ppm. No peak due to the allenic moiety from possible metal-catalyzed isomerization of the propargyl group is seen in the NMR spectrum. The ratios of the two comonomers in copolymers **1a**−**1d** were calculated using the methylene protons at 4.62 ppm (OCH_2−C≡C within propargyl acrylate fraction) and at 3.61 ppm (from methyl methacrylate fraction). Methyl methacrylate is more reactive than propargyl acrylate in this radical polymerization reaction as proven by the higher number of methyl methacrylate fragments incorporated in the copolymers. The relative ratio of propargyl acrylate to methyl methacrylate in the copolymers ranged from 1/32.5 to 1/0.8 (Table 1), as determined from the NMR data.

Analyses by gel permeation chromatography indicated that copolymers **1a**−**1d** had weight-average molecular weights ranging from 54 000 to 350 000 (Table 1). Homopolymer **1e** could only be obtained in relatively low molecular weight (88 000) with a large polydispersity (8.3), indicating chain termination likely caused by side reaction of the ethynyl group. The onset temperatures for 5% weight loss in nitrogen for all the polymers were determined by thermogravimetry (TG) to be in a range of 285 °C (**1a**) to 335 °C (**1e**). Differential scanning calorimetry (DSC) revealed the glass transition temperatures for all the polymers in a range of 37 °C (**1d**) to 115 °C (**1a**) (Table 1). Like polymer **1c** shown in Figure 1 (trace a), these acetylene-containing polymers are thermally reactive or cross-linkable, as their DSC traces displayed two exothermic peaks at about 150 °C for the first exotherm and at about 260 °C for the second one.

To demonstrate photo-cross-linking of these polymers in the presence of $W(CO)_6$, three experiments were

---

* Corresponding author. E-mail: wangw@ccs.carleton.ca.

10.1021/ma034657r CCC: $25.00

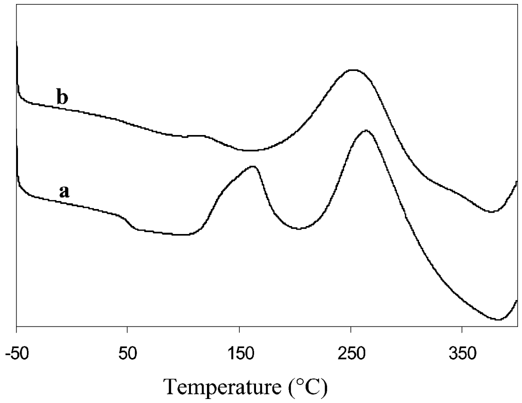


Figure 1. DSC traces of polymer **1c**: (a) before UV irradiation and (b) after UV irradiation for 60 min at 70 °C.

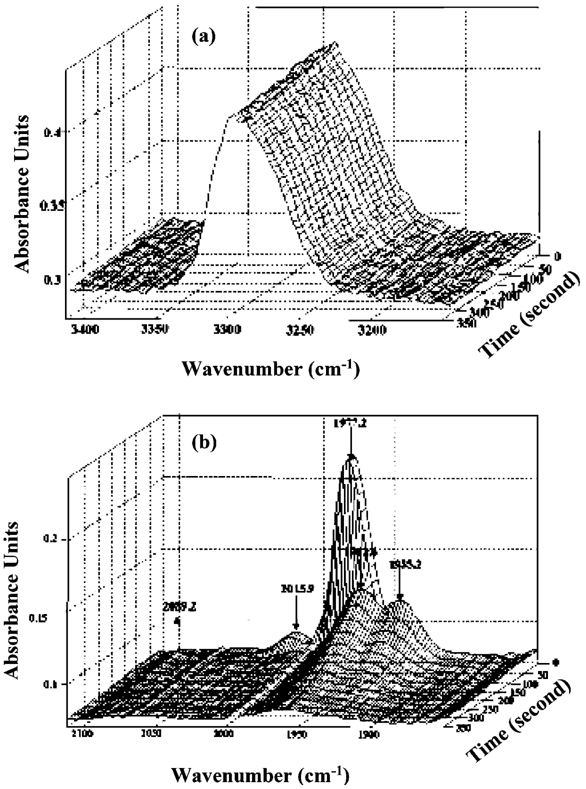


Figure 2. FTIR spectra of polymer **1c** during the initial stage of photo-cross-linking (0−350 s) for (a) the ≡C−H stretch and (b) carbonyl peaks of $W(CO)_6$ and alkyne−$W(CO)_5$ species.

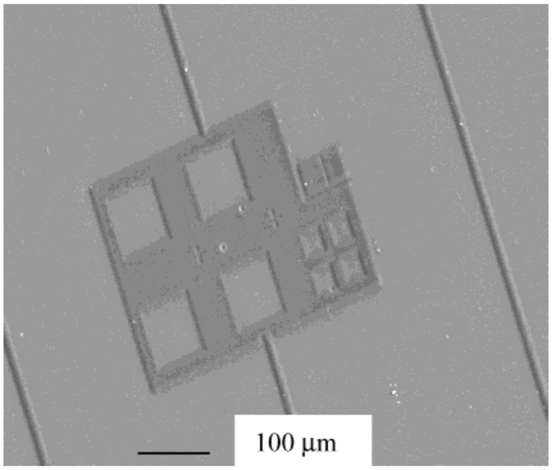


Figure 3. SEM micrograph of a patterned film of polymer **1c** (2 µm thick film, doped with 5 mol % of $W(CO)_6$, irradiated at 320−390 nm with a 3500 mW/cm^2 intensity). Darker areas are covered with polymers.

carried out using polymer **1c** as a representative example. First, irradiation of a polymer solution in TCE (6.5% w/v) at 320−390 nm using a 100 mW/cm^2 intensity beam (Ultracure 100SS Plus/Novacure system) did not yield any polymer gels. After doping the polymer solution with 5 mol % of $W(CO)_6$ and exposure to UV light for 30 s, a gelation clearly occurred. Polymer films doped with 5 mol % of $W(CO)_6$ were then irradiated (320−390 nm, 3500 mW/cm^2) for 60 min and were found to be completely insoluble in organic solvents. Infrared analysis was performed on polymer films that were cast on NaCl plates and exposed to UV light showed that the acetylene absorption at 3300 cm^{-1} (≡C−H) greatly decreased by nearly 66.6% after 60 min (Figure 2a). UV exposure of the undoped polymer film did not result in any changes in the IR spectrum. The DSC analysis on polymer **1c** also revealed a significant change in polymer structures before and after UV irradiation (for 60 min at 70 °C), as the photoirradiated polymer had no T_g and a negligible exotherm at 150 °C (Figure 1, trace b). It can be noticed that the second exotherm around 260 °C did not change, suggesting that the structures thermally at lower temperatures (150 °C) and photochemically at ambient temperatures are quite similar and can be further thermally cross-linked at higher temperatures. Finally, direct photopatterning of polymer **1c** (doped with 5 mol % of $W(CO)_6$) on a silicon wafer was achieved by UV irradiation (3500 mW/cm^2) of an approximately 2 µm thick film through a contact mask (Figure 3). In comparison, the undoped polymer films could not be patterned in the same way.

Marshall et al.[15] showed that UV photolysis of $W(CO)_6$ in the presence of an alkyne resulted in the formation of a η^2-alkyne tungsten pentacarbonyl complex [$(\eta^2\text{-RC}{\equiv}\text{CR}')W(CO)_5$] that rearranges to a vinylidene derivative [$R(H)C{=}C{=}W(CO)_5$].[12] This step was proven to be the initiation step in the polymerization of alkynes. Prolonged irradiation with UV light and coordination to another alkyne molecule resulted in the formation of tungsten tetracarbonyl species, which triggered the photocatalytic cycle. The IR bands of all these catalytic intermediates are reported and can be easily assigned.[12] In our case, the initial IR spectrum of $W(CO)_6$-doped polymer films showed a sharp peak at 1977 cm^{-1} with a small shoulder at 2016 cm^{-1} (Figure 2b). UV photolysis at 320−390 nm for 40 s at ambient temperature generated the alkyne pentacarbonyl derivatives having three characteristic bands at 1935 cm^{-1} (medium), 1962 cm^{-1} (strong), and 2089 cm^{-1} (weak). The peak positions and relative intensities correspond well to the reported alkyne−$W(CO)_5$ fragments.[12] The tungsten tetracarbonyl complexes that are known to be intermediates in the alkyne polymerization[9c] could not be detected in our IR study, due to the known fact that they have a very short lifetime at ambient temperatures. Prolonged irradiation (>1000 s) of the polymer films resulted in the nearly complete loss of CO ligands from the tungsten carbonyl species.

In conclusion, efficient photo-cross-linking of acrylate-type polymers having the ethynyl groups in the side chain in the presence of $W(CO)_6$ has been demonstrated. This new photo-cross-linkable system serves as a model for further development of various types of photo-cross-linkable polymers, especially those that have better optical properties and stability than PMMA, containing the alkyne groups in the main chain, side chain, and chain ends, in the presence of a small amount of $W(CO)_6$ or other catalysts such as $Mo(CO)_6$, $Cr(CO)_6$,[9] and $(CO)_4W{=}C(OCH_3)C_4H_7$[10] that can promote the acetylene polymerization. Detailed studies on the relationships between the polymer structures, acetylene content, metal catalysts, and kinetics of photo-cross-linking reactions are now in progress.

Acknowledgment. This work was financially supported by the Natural Sciences and Engineering Research Council of Canada. C. Badarau acknowledges the financial support of the Ontario government through the Ontario Graduate Science and Technology Scholarship and Nortel Networks.

References and Notes

(1) Hong, S. I.; Joo, S. Y.; Kang, D. W. In *Desk Reference of Functional Polymers: Syntheses and Applications*; Arshady, R., Ed.; American Chemical Society: Washington, DC, 1997; p 293.

(2) (a) Ranby, B.; Qu, B.; Shi, W. In *Polymeric Materials Encyclopedia*; Salmone, J. C., Ed.; CRC Press: New York, 1996; Vol. 7, p 5155. (b) Packowski, J. *Polymeric Materials Encyclopedia*; Salmone, J. C., Ed.; CRC Press: New York, 1996; Vol. 7, p 5142. (c) Green, C. E.; Starck, B. P. *J. Macromol. Sci., Rev. Macromol. Chem.* **1981–82**, *C21* (2), 187. (d) Holden, D. A. *Encyclopedia of Polymer Science and Engineering*; John Wiley & Sons: New York, 1990; Vol. 11, p 126.

(3) Landis, A. L.; Bilow, N.; Boschan, R. H.; Lawrence, R. E.; Aponyi, T. J. *Polym. Prepr.* **1974**, *15*, 533.

(4) Kellman, R.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2033.

(5) Jabloner, H.; Cessna, L. C. J. *Elastomers Plast.* **1974**, *6*, 103.

(6) Havens, S. J.; Hergenrother, P. M. *Polym. Prepr.* **1983**, *24* (2), 16.

(7) Kovar, R. F.; Ehlers, G. F.; Arnold, F. E. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1081.

(8) Swanson, S. A.; Fleming, W. W.; Hofer, D. C. *Macromolecules* **1992**, *25*, 582.

(9) (a) Masuda, T.; Kuwan, J.; Yamamoto, K.; Higashimura, T. *Polym. Bull. (Berlin)* **1980**, *2*, 823. (b) Masuda, T.; Yamamoto, K.; Higashimura, T. *Polymer* **1982**, *23*, 1663. (c) Shayne, Y.; Shulman, P. M.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 6739.

(10) (a) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, L. *J. Am. Chem. Soc.* **1983**, *105*, 3064. (b) Liaw, D. J.; Hu, K. R.; Chiang, H. H.; Kang, E. T. *Polym. J.* **1995**, *27*, 262.

(11) Tamura, K.; Masuda, T.; Higashimura, T. *Polym. Bull. (Berlin)* **1994**, *32*, 289.

(12) (a) Szymanska-Buzar, T. *Coord. Chem. Rev.* **1997**, *159*, 205. (b) Xu, K.; Peng, H.; Lam, J. W. Y.; Poon, T. W. H.; Dong, Y.; Xu, H.; Sun, Q.; Cheuk, K. K. L.; Saldhi, F.; Lee, P. P. S.; Tang, B. *Macromolecules* **2000**, *33*, 6918.

(13) Cohen, M. S.; Karlan, S. I. U.S. Patent 3,254,115, May 31, 1966.

(14) A typical polymerization procedure is given for polymer **1c.** An Ace pressure tube (10 mL) was charged with propargyl acrylate (0.549 g, 0.005 mol), methyl methacrylate (0.500 g, 0.005 mol), benzoyl peroxide (0.3 wt %), and 2.1 mL of benzene. Nitrogen was bubbled through the reaction mixture for 30 min, and then the tube was sealed. After heating at 70 °C for 4 h the viscous solution was diluted with chloroform and precipitated in hexane (250 mL). The white powdered polymer was filtered and dried under vacuum at 45 °C (yield 19%).

(15) Szymanska-Buzar, T.; Dows, A. J.; Green, T. M.; Marshall, A. S. *J. Organomet. Chem.* **1995**, *495*, 163.

MA034657R