

STM Observation of Single Molecular Chains of π -Conjugated Polymers

Hitoshi Kasai, Hiroyuki Tanaka,[†] Shuji Okada, Hidetoshi Oikawa,
Tomoji Kawai,[†] and Hachiro Nakanishi*

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577

[†]The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047

(Received March 18, 2002; CL-020245)

Single molecular chains of π -conjugated polymers such as polythiophene and polydiacetylene were clearly observed by STM, and their molecular structures and/or conformation were discussed in relation to bonding characteristics. It should be noted that even molecular weight could be determined using well-resolved STM images.

Nanomaterials have vigorously been investigated all over the world by virtue of the remarkable progress in scanning tunneling microscopy (STM) techniques. Recently, the STM observation has made it possible to identify single molecules of polymers and organics.^{1,2} However, most of such researches were on the aggregated molecules like those made by CVD, LB and SAM methods. Therefore, any information about the flexibility of single polymer chain has not been obtained, although the optical and electrical properties of π -conjugated polymers are much dependent on main chain structure. In this paper, we discuss the structure of single molecular chains of π -conjugated polymers stuck on a Cu substrate.

The π -conjugated polymers used in this study were poly(3-hexylthiophene-2,5-diyl) (PHT) and poly(5,7-dodecadiyne-1,12-diyl bis(*N*-(butyloxycarbonylmethyl)carbamate) (poly-4BCMU), as shown in Figure 1. The regioregular PHT (M_r : 86000)³ was purchased from Aldrich. 4BCMU was synthesized according to the literature.⁴ Poly-4BCMU was obtained by the solid-state photopolymerization of 4BCMU nanocrystals.

The sample for STM observation was prepared as follows.

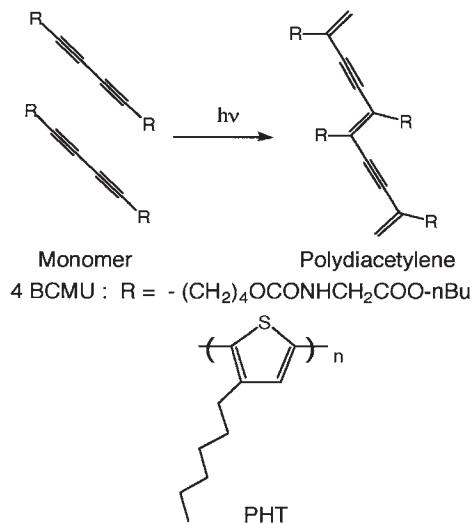


Figure 1. The π -conjugated polymers used for STM observation in this study.

The chloroform solution of target compounds (10^{-6} M) was sprayed under high vacuum on the Cu(111) surfaces at room temperature using the pulse injection technique.⁵ After the deposition, the Cu(111) substrate was transferred into the STM chamber to observe STM images. The STM observation was performed using USM-602S2 (Unisoku Co., Osaka, Japan), with electrochemically etched Pt-Ir tips, at liquid nitrogen temperature. The images were typically taken with a sample bias of -5 to 5 V and a tunnel current of 1 pA in a temperature range of 92 to 94 K in UHV at 1×10^{-10} Torr.

Figure 2 shows a clear STM image of PHT on Cu(111) substrates. It was considered that the bright spheres exhibit hexyl group attached to the thiophene rings, because their pitch is 7.8 Å in accordance with the distance obtained by molecular mechanics (MM) calculation. In the straight portion such as A in Figure 2, the polymer chain must be composed of rigid all trans conformation of thiophene rings as is the inserted chemical structure for A. Incidentally, the yellow points of the chemical structure correspond to sulfur atoms. Amazingly, it was found that the bending angle of the main chain was fixed to either about 120 or 60 degree such as B or C in Figure 2. MM calculation indicated that the molecular structures of the B and C can be assigned to successive conformers of thiophene rings: When three or five thiophene rings continuously keep cis conformation, the bending

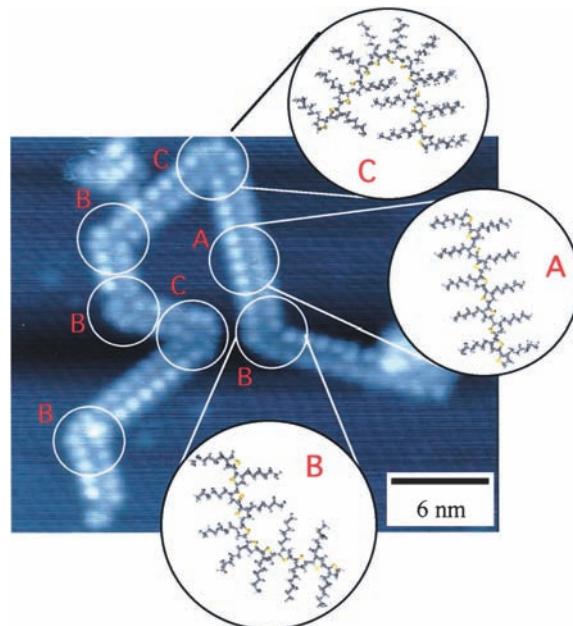


Figure 2. STM image of thiophene polymer on Cu(111) substrates.

angle becomes about 120 or 60 degree as the inserted chemical structure for B or C in Figure 2. This result can be understood by turnover phenomena of one or two thiophene rings from the all-trans conformation, when the polymer was stuck onto the substrate.

The number of monomer units in this polymer was definitely counted to be 119 by spheres, and therefore it is determined that the molecular weight of this PHT molecule is 19788. Yase et al. reported on molecular orientation of substituted phthalocyaninato-polysiloxanes in Langmuir-Blodgettes films. In the paper, the degree of polymerization and/or the molecular weight of phthalocyanines in the films were estimated from transmission electron microscopic images.⁶ Our STM would also be very powerful tool to determine the absolute molecular weight of polymer.

Figure 3(a) shows STM images of polydiacetylene chains of poly-4BCMU which were obtained from the nanocrystals with about 200 nm in size. The polymer nanocrystals with well-defined size were fabricated in water by the conventional reprecipitation method,⁷⁻⁹ succeeding UV irradiation to take place solid-state polymerization, and were collected on Milipore filter with

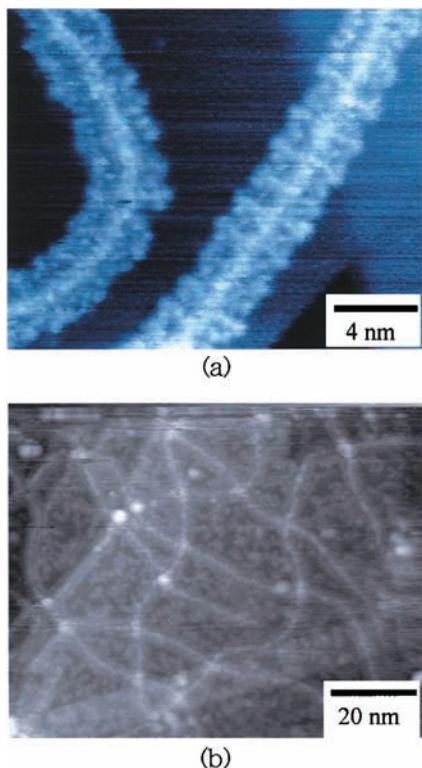


Figure 3. STM image of polydiacetylene chains of poly(4BCMU) on Cu(111) substrates.

appropriate pore size. After dissolving them in chloroform, the yellow solution was used to prepare the sample for STM observation. Compared with the thiophene polymer, it was difficult to observe polydiacetylene chains clearly. However, it turned out that bright center lines and their surrounding parts correspond to main and side chains of the polydiacetylene, respectively. The maximum width of side chain in each side of polymer was about 1.7 nm. This is almost the same value as that for the extended substituent by MM calculation.

The length of a total polydiacetylene chain seemed to be longer than 160 nm, as seen from Figure 3(b). This is well in the range of conceivable maximum length of the polymer chain, i.e. 200 nm. There has been a long standing discussion on the relation of the color and the structure of polydiacetylene in solution.^{10,11} The color of poly-4BCMU in single crystal is deep blue, and the molecular structure is the planer rod-like chain. However, the yellow color of the solution was estimated to be due to a warm-like twisting, or the deterioration of π -conjugation by kink-structures. Interestingly, it was found, for the first time, that polydiacetylene chain could make a smooth curve with gradual twisting. This must be the reason for the yellow color in solution.

In conclusion, the structure of single molecule chains of π -conjugated polymers could be observed by use of the STM. And it was demonstrated that this technique is very useful for determination of the absolute molecular weight of polymer and also for discussing the structure-property relationship.

References

- 1 “Scanning Tunneling Microscopy II: Further Applications and Related Scanning Techniques,” ed. by R. Wiesendanger and H.-J. Gütterdt, Springer, Berlin (1992), Vol. 28.
- 2 C. J. Chen, “Introduction to Scanning Tunneling Microscopy,” Oxford University Press, London (1993).
- 3 T.-A. Chen, X. Wu, and R. D. Rieke, *J. Am. Chem. Soc.*, **117**, 233 (1995).
- 4 G. N. Patel, Y. P. Khanna, D. M. Ivory, J. M. Sowa, and R. R. Chance, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 899 (1979).
- 5 H. Tanaka and T. Kawai, *J. Vac. Sci. Technol., B*, **15**, 602 (1997).
- 6 K. Yase, S. Schwiegk, G. Lieser, and G. Wegner, *Thin Solid Films*, **210**, 22 (1992).
- 7 H. Kasai, H. S. Nalwa, S. Okada, H. Matsuda, H. Oikawa, N. Minami, A. Kakuta, K. Ono, A. Mukoh, and H. Nakanishi, *Jpn. J. Appl. Phys.*, **31**, L1132 (1992).
- 8 H. Nakanishi and H. Kasai, *ACS Symp. Ser.*, **672**, 183 (1997).
- 9 R. Iida, H. Kamatani, H. Kasai, S. Okada, H. Oikawa, H. Matsuda, A. Kakuta, and H. Nakanishi, *Mol. Cryst. Liq. Cryst.*, **267**, 95 (1995).
- 10 B. Chu and R. Xu, *Acc. Chem. Res.*, **24**, 384 (1991).
- 11 H. Oikawa, T. Korenaga, S. Okada, and H. Nakanishi, *Polymer*, **40**, 5993 (1999).