Intrinsic Nonsolvent Polymerization Method for Synthesis of Highly Stretchable and Highly Conductive Polyacetylene Films

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We present a novel solvent-free polymerization method that gives highly stretchable and highly conductive polyacetylene films. It has been currently demonstrated that mechanical strength as represented by the Young's modulus and tensile strength is a central criterion[1,2] to evaluate the stretchability of a polyacetylene film and therefore the electrical conductivity of the stretched film upon chemical doping. For an interfacial acetylene polymerization, it is of primary importance to use a high concentration of catalyst.[3,4] Recently, we developed a polymerization procedure called the "solvent evacuation" method.[1] Therein, the solvent used for the Ziegler–Natta catalyst is evacuated by dynamic pumping just before introduction of acetylene gas into a polymerization flask. This method is found to be promising to synthesize polyacetylene films with a high density and high stretchability, provided the catalyst is pretreated by so-called high-temperature aging.[1,5,6]

The present method also lies in extending the solvent-free acetylene polymerization. Neat triethylaluminum ($AlEt_3$) is added dropwise to neat tetra-*n*-butoxytitanium ($Ti(O\text{-}n\text{-}Bu)_4$) in a Schlenk flask, keeping the temperature below 0 °C. The catalyst is then subjected to aging at room temperature for 1 h, followed by high-temperature aging at 150 °C for 1 h. Subsequently, the flask is degassed and the catalyst is coated on the inner wall of the flask by rotating it. After the flask is cooled to −78 °C, acetylene gas is introduced. The polymerization is carried out for 0.5–1 h. The polyacetylene film synthesized is washed several times by toluene cooled to −78 °C and dried through vacuum pumping. Since the procedure from the catalyst preparation to the end of the polymerization is completely free from solvent, it can be called an "intrinsic nonsolvent" polymerization method.

Polyacetylene films thus obtained are black and dull in color with no metallic luster, as observed in films prepared by the solvent evacuation method. Such an appearance presents a striking contrast to typical S-type films with a metallic luster synthesized using a room-temperature aged catalyst with solvent.[3] Since the macroscopic properties of the polyacetylene film depend on the preparative conditions, especially the activity of the catalyst,[4,7] it is worthwhile to grasp global features for relationships between some properties of the present film and a representative parameter in preparing the catalyst solution such as the Al/Ti ratio, the concentration ratio between the catalyst, $Ti(O\text{-}n\text{-}Bu)_4$, and the cocatalyst, $AlEt_3$. Figure 1 shows the mechanical stretchability of as-grown films as a function of the Al/Ti ratio. Here, the mechanical stretchability is defined as the elongation at break, and it is expressed by the draw ratio (l/l_0) at the break point, in which l_0 and l are film lengths before and after the stretching, respectively. The stretchability increases up to 6–9 in draw ratio (l/l_0) with increasing Al/Ti ratio and then decreases above an Al/Ti ratio of 6. Figure 2 shows the electrical conductivity of stretched iodine-doped films versus the Al/Ti ratio. The doping was carried out by

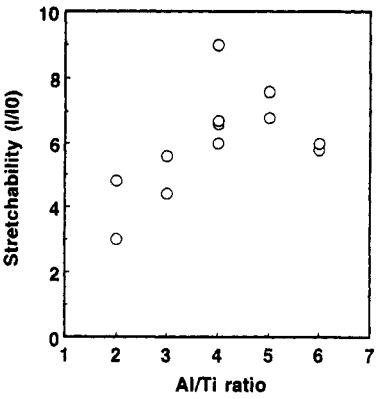

Figure 1. Stretchability represented by draw ratio (l/l_0 at break point) of as-grown $(CH)_x$ film vs Al/Ti ratio. Here, l_0 and l are film lengths before and after the stretching, respectively.

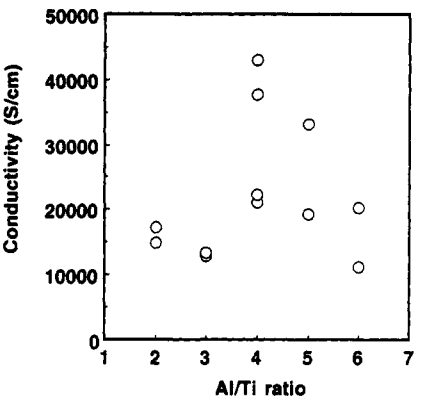

Figure 2. Electrical conductivity of iodine-doped stretched $(CH)_x$ film vs Al/Ti ratio. The conductivities are parallel to the stretching direction.

exposing the mechanically stretched film to iodine vapor, and the electrical conductivity of the film was measured in terms of parallel conductivity along the stretched direction by a four-probe method at room temperature. In Figure 2 there is apparently no distinct relationship between the conductivity and the Al/Ti ratio. Note that the data points shown in each figure are from different batch samples and that there are inevitably sample-to-sample variations. This is the usually encountered case and is mainly due to the multifaced character and behavior of the $Ti(O\text{-}n\text{-}Bu)_4$–$AlEt_3$ catalyst system.[4] However, one can find that a favorable Al/Ti ratio to produce a highly conductive polyactylene film is 4–5, consistent with the result of Figure 1. Especially, the as-grown films prepared with an Al/Ti ratio of 4 have a high cis content of 85–95%, and they also have a high bulk density of 1.0–1.1 g/cm^3, very close to the true density of 1.16 g/cm^3.[8] Mechanical stretching of these films followed by iodine doping yields high electrical conductivities of 2.2×10^4 to 4.3×10^4 S/cm. These values are comparable to or higher by 2 times than those of films prepared by the solvent evacuation method.[1]

It is of interest that the Al/Ti ratio of 4–5 is quite in contrast to the value of 2, which has been optimized for the high-temperature aged catalyst with solvent.[1,6,9,10] Why is the optimal ratio 4–5 and not 2 for the nonsolvent case, in spite of the usage of the high-temperature aged catalyst? One may point out as a plausible interpretation that free $AlEt_3$ molecules remaining even after the complexation between $Ti(O\text{-}n\text{-}Bu)_4$ and $AlEt_3$ might exist as if they were solvent molecules toward the catalytic complexes[11–14] and contribute to stabilize them through so-called solvation. This condition permits the complexes to be homogeneously distributed in the catalyst solution. Thereby, a morpho-

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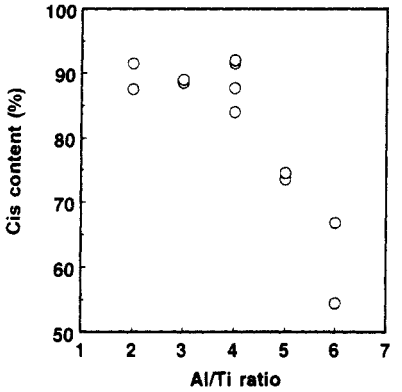

Figure 3. Cis content of as-grown $(CH)_x$ film vs Al/Ti ratio.

logically homogeneous polyacetylene film suitable for mechanical stretching can be produced. In other words, the present method needs an excess of $AlEt_3$, i.e., by 4–5 times the $Ti(O\text{-}n\text{-}Bu)_4$ concentration, so that the $AlEt_3$ can serve as a solvent toward the catalytic complexes. In fact, the potential utility of trialkylaluminum as solvent may be supported by its dielectric constant; the values for AlR_3 (R = Et, Pr, and *i*-Bu) are in the range 2.005–2.580, which are close to those of the usually employed polymerization solvents *n*-hexane (1.902), decalin (2.175), cumene (2.222), and toluene (2.237).

Next let us examine the cis content of the $(CH)_x$ film. It has been implicitly believed so far that the as-grown film with higher cis content exhibits a higher electrical conductivity upon doping after mechanical stretching. Therefore, the cis content has been one of the indexes to evaluate the quality of $(CH)_x$ film. Figure 3 shows the changes of cis content of the as-grown films as a function of Al/Ti ratio. The cis-rich films of 85–95% in cis content are produced at an Al/Ti ratio of 2–4. However, the cis content decreases notably above an Al/Ti ratio of 5. This result implies that the most favorable Al/Ti ratio for cis content is 2–4. From comparison of Figures 1–3, it can be argued that the most favorable Al/Ti ratios for cis content are not always those for mechanical stretchability and electrical conductivity. In other words, the $(CH)_x$ films of high cis content do not always exhibit high stretchability and/or high electrical conductivity upon iodine doping.

Lastly, it should be emphasized that the present solvent-free method using the versatile $Ti(OR)_4$–AlR_3 catalyst[15,16] is widely applicable to other kinds of polymerizations that have hitherto used a solvent for preparation of the catalyst and the polymerization reaction.

Further studies are underway to extend catalyst systems by changing alkyl and/or alkoxy substituents in aluminum and titanium compounds.

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References and Notes

(1) Akagi, K.; Suezaki, M.; Shirakawa, H.; Kyotani, H.; Shimomura, M.; Tanabe, Y. *Synth. Met.* **1989**, *28*, D1.
(2) Cao, Y.; Smith, P.; Heeger, A. J. *Polymer* **1991**, *32*, 1210.
(3) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11; **1975**, *13*, 1943.
(4) Chien, J. C. W. *Polyacetylene—Chemistry, Physics, and Material Science*; Academic Press: Orlando, FL, 1984; Chapter 2.
(5) (a) Pedretti, U.; Perego, G.; Lugli, G. (Assoreni), *Ital. Patent Appl.* No. 22722/A82, 1982. (b) Lugli, G.; Pedretti, U.; Perego, G. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 129. (c) Lugli, G.; Pedretti, U.; Perego, G. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 43.
(6) Naarrmann, H.; Theophilou, N. *Synth. Met.* **1987**, *22*, 1.
(7) Schen, M. A.; Karasz, F. E.; Chien, J. C. W. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2287.
(8) Abadie, M. J. M.; Hacene, S. M. B.; Cadene, M.; Rolland, M. *Polymer* **1986**, *27*, 2003.
(9) Shirakawa, H.; Zhang, Y.-X.; Mochizuki, K.; Akagi, K.; Kyotani, K.; Tanabe, K. *Synth. Met.* **1991**, *41*, 13.
(10) The optimal Al/Ti ratio in the solvent evacuation method is 2,[1] because in this method both the preparation and the aging of catalyst are carried out with an organic solvent such as toluene and cumene, although the solvent is evacuated before polymerization.
(11) Djabiev, T. S.; Sabirova, R. D.; Shilov, A. E. *Kinet. Katal.* **1964**, *5*, 441.
(12) Takeda, M.; Iimura, K.; Nozawa, Y.; Hisatome, M.; Koide, N. *J. Polym. Sci., Part C* **1968**, *23*, 741.
(13) (a) Hirai, H.; Hiraki, K.; Noguchi, I.; Makishima, M. *J. Polym. Sci., Part A* **1970**, *8*, 147. (b) Hirai, H.; Hiraki, K.; Noguchi, I.; Inoue, T.; Makishima, M. *J. Polym. Sci., Part A* **1970**, *8*, 2393.
(14) (a) Akagi, K.; Hashimoto, D.; Shirakawa, H.; Isoya, J. *Polym. Commun.* **1990**, *31*, 411. (b) Akagi, K.; Hashimoto, D.; Shirakawa, H.; Isoya, J. *Synth. Met.* **1991**, *40*, 197.
(15) (a) Ziegler, K. *Angew. Chem.* **1964**, *76*, 545. (b) Natta, G. *Science* **1965**, *147*, 261.
(16) Odian, G. *Principles of Polymerization*, 2nd ed.; Wiley: New York, 1981; Chapter 8.