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Preparation and Properties of Organic Polymer Ferromagnet with Indigo Unit

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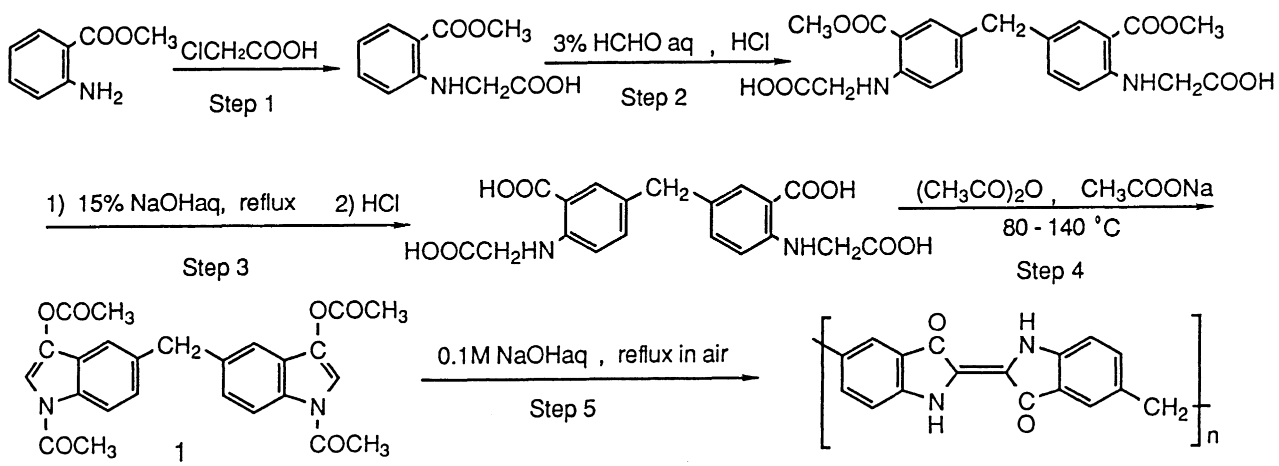
A new organic polymer ferromagnet with indigo unit in the main chain was prepared and its magnetic properties were examined. Resulting polymer contained the fraction which attracted to a permanent magnet and it showed a definitive hysteresis loop at room temperature.

Constructing an organic ferromagnet is now greatly interested. After theoretical considerations[1,2] and the preparation[3] of high spin molecule for about two decades, the first organic ferromagnet was published in 1987.[4-6] However, ferromagnetism has not yet clearly been observed in any purely organic compounds at room temperature because of their irreproducibility, very low magnetization, and so on. That is, the doubt as to whether a pure organic molecule really becomes a ferromagnet is yet questionable. In the course of the continuing works on captodative substituted persistent radical,[7] we found that the polymer with indigo moiety in the main skeleton was attracted to a permanent magnet. Here we report the preparation of a reproducible organic polymer ferromagnet with a definitive hysteresis loop at room temperature.



Scheme 1.

Preparation of an organic polymer ferromagnet is represented in Scheme 1, where the reactions were carried out in quartz vessels and the compounds were treated with sapphire tweezers and a teflon coated spatula to avoid the contamination with the high spin metals such as Fe, Co, and Ni. Steps 1, 3, 4, and 5 are similar to the reactions already employed in the synthesis of conventional monomeric indigo.[8,9] The step 2 is similar to the reaction of phenol resin synthesis. The last step of the reaction is an aerial oxidative polymerization giving indigo units in a polymer chain, which was carried out in an inhomogeneous slurry medium because of the poor solubility of **1**. The yield of each step was determined to be 52, 90, 98, 97, and 97% respectively. Resulting polymer was brown or black and consists of small grain (ca. 5%) and larger hard mass (ca. 95%) portions. The almost all small grain (part A) and 10% of the hard mass (part B) were quickly attracted toward a permanent bar magnet (Alnico, ca. 1200G) not only on the water surface but also on a desk as is indicated in Fig.1. In this Figure, we can clearly see that the polymer is selectively attracted to the site of a higher magnetic field, i.e., the edge of a permanent magnet. The polymer was stable and attracted to the magnet even by the heating at 200 °C. It is noted that the amount of the magnet attracted fraction in the present polymer is larger than that in other organic polymers and its reproducibility was 100% in 30 runs. For example, nitroxy[4] and triaminobenzene[6] polymers contained only 0.1 and 2% of such fraction in the resulting polymers respectively, and they were not very reproducible.

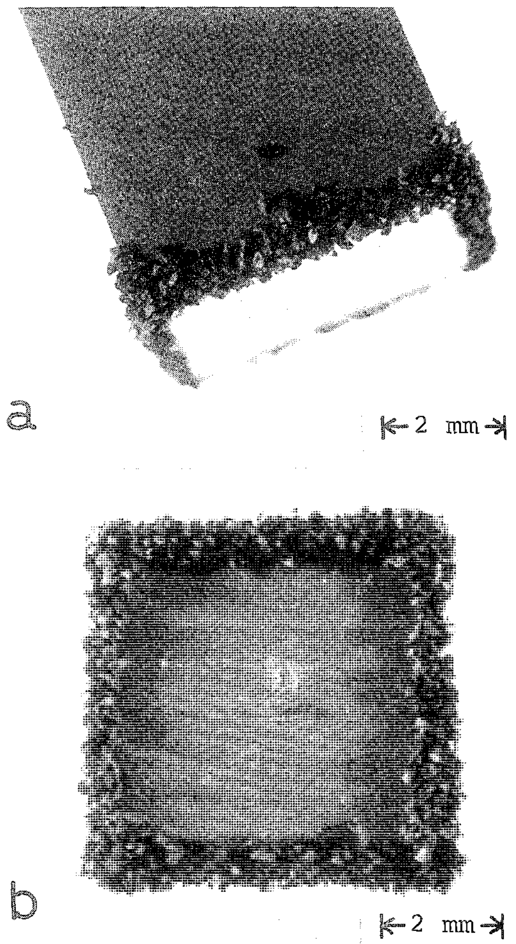


Fig.1. Photographs of part A attracted toward a permanent magnet (Alnico, ca. 1200 G) at room temp. Taken a photograph (a) from the side and (b) under the magnet.

Since the structure of the polymer was not clearly identified because of its poor solubility in most organic solvents, it was speculated from the IR spectra. The spectra (diamond cell, resolution of 4 cm^{-1}) of both parts A and B were nearly identical, and they are similar to a commercially available monomeric indigo as is shown in Fig.2. The absorption due to C=O streching at 1760 and 1700 cm^{-1} observed in **1** (identification of **1** by ^{1}H-NMR in CDCl$_3$: δ2.36 (s, 3H), 2.59 (s, 3H), 4.19 (s, 2H), 7.25 (d, J= 9 Hz, 1H), 7.35 (s, 1H), 7.69 (s, 1H), and 8.37 ppm (d, J= 9 Hz, 1H)) is shifted to near 1620 cm^{-1} in polymeric and monomeric indigos. This is a characteristic peak to an indigo.[10] Therefore, the polymer has essentially an indigo skeleton. However, slightly different absorptions at 1400-700 cm^{-1} and broad bands near 3400 and 1620 cm^{-1} in spectrum b seem to suggest that the polymer is not constracted only by the repetition of a conventional coplanar trans indigo, and contains irregular fragments, hydrogen bond, and so on. Inhomogeneous reaction and poor solubility of the resulting polymer make it difficult to complete the reaction and purify the polymer.

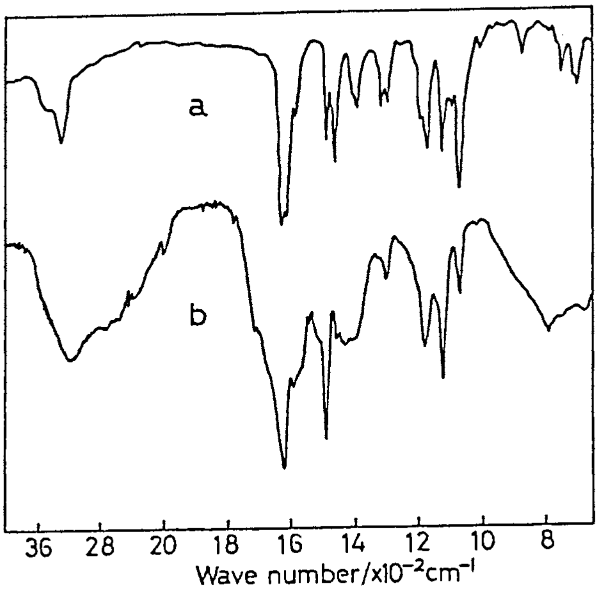


Fig.2. Infrared spectra of (a) monomeric indigo and (b) indigo polymer (part A). Measured by (a) KBr pellet and (b) diamond cell.

Figure 3 represents the magnetic hysteresis curve of the part A recorded on a vibrating sample magnetometer (Riken Denshi, VSM model BHV-30) at 25 °C. It is also noted that a definitive hysteresis loop and a magnetic saturation are observed even in small grain. The saturation magnetization (H_s), residual magnetization, and coercive force are determined to be 0.7 emu/g, 0.08 emu/g, and 120 Oe respectively, which are very high among organic ferromagnets. The expected H_s value per repeat unit would be 5583 emu/equiv. Thus the

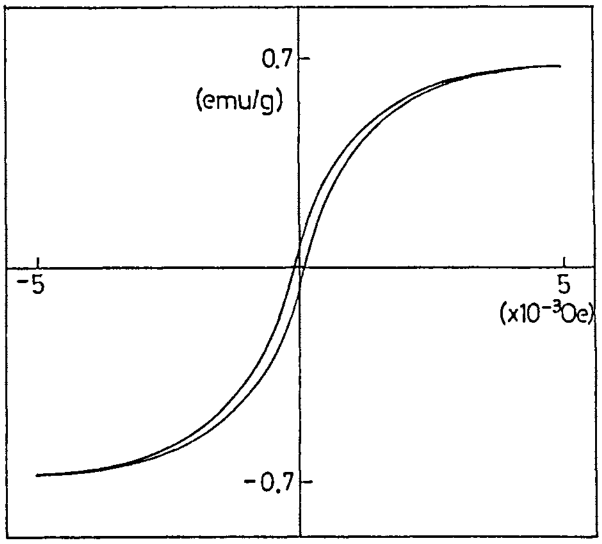


Fig.3. Magnetic hysteresis curve of indigo polymer (part A) at 25 °C.

value of 0.7 emu/g or 192 emu/equiv. indicates that 3.4% of the sample is ferromagnet. Transition metal content in parts A and B was determined by ICP atomic emissions spectrography (Leeman Labs, model PS-1000UV) to be 26 and 28 ppm respectively for Fe and less than 1 ppm for Co and Ni. No such metals were detected in X-ray fluorescent analysis. The H_s value is equivalent to about 3200 ppm Fe, two orders of magnitude greater than that detected by ICP. Therefore, such a small amount of Fe is negligible in an atmospheric condition, and the magnetism should be attributable to the organo ferromagnetic structure itself. Although poor solubility of the polymer prevents a detail structural analysis, its spin state is roughly speculated as follows. The main feature of the ESR spectrum of both parts at 25 °C is a large broad line due to a high spin state and a relatively small sharp line with g= 2.0048 and ΔH_{msl}= ca. 7.0 G due to a paramagnetic absorption. Such higher g value than free carbon radical (g= 2.002-2.003) suggests that probably a spin is mainly on the central olefinic carbon of the indigo unit and it is stabilized by the captodative (C=O and NH) effect.7,11) Then the spins are linked to one another by odd number of conjugated carbons, i.e., 9 carbons, which satisfies the rule of spin polarization2) and results in a positive exchange interaction of intramolecular spins. Intermolecular such interaction arises from a reasonable stacking of each polymer chains probably by a cross-linking or a hydrogen bond as is known in dimeric indigo.12) More detail studies are now in progress.

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