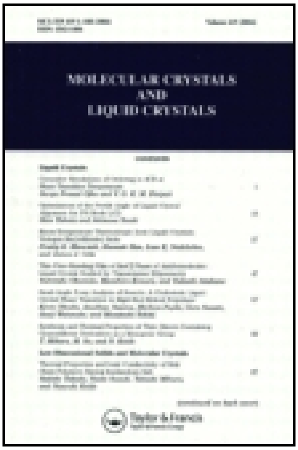

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SYNTHESIS AND MAGNETIC STUDIES OF POLYDIACETYLENE WITH α-NITRONYL NITROXIDE AS SIDE GROUP

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Abstract The diacetylene with stable α-nitronyl nitroxide as side group was synthesized and polymerized by heating. The magnetic properties of the polymer were measured, and it was assumed that this organic polymer is in the spin glass state.

INTRODUCTION

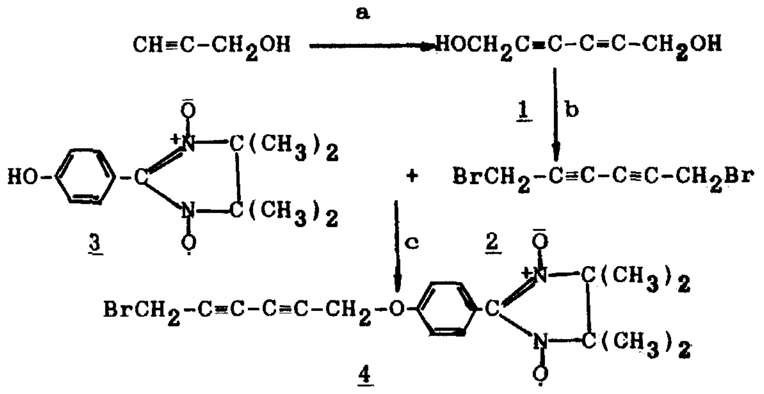
The pursuit of molecular-based organoferromagnet has developed into a major focus of modern chemistry[1]. A lot of scientists are attracted to this research field because organic materials have many advantages compared with inorganic compounds. Interesting results have been obtained[2]. Among them, the most promising is the first reported organic polymer ferromaget-Poly((4,4'-BUTADIYNE-1,4-DIYL)-BIS-(2,2,6,6-TETRAMETHYL-4-HYDROXY-PIPERIDIN-1-OXYL)) in 1987[3]. After that, Chinese and Japanese scientists have successively repeated the experiment and observed the similar ferromagmetic behavior[4]. On the other hand, American scientists have confirmed that the observed ferromagetism was due to the transition metal contamination[5]. Although some theoretical model and theoretical calculation have been put out to explain this magmetic phenomenon[6], the controversy can not be settled at present. Meanwhile, some organic stable radicals, for example, 2-(4-NITROPHENYL)-4,4,5,5-TETRAMETHYL-4,4-DIHYDRO-1H-IMIDAZOLYL-1-OXY-3-OXIDE))[7], have been found to show ferromagnetic properties.

In this paper, the synthesis and magnetic studies of the new polydiacetylene with α-nitronyl nitroxide as side group were reported.

PREPARATION AND CHARACTERIZATION

In Scheme 1, compounds 1,2,3 were prepared according to literatures[8], and compound 4 was synthesized by the following procedure.

0.48g 3 dissolved in absolute methanol (20ml). 0.11g KOH was added to the above solution and stirred for 2hrs at r.t. Then, the solvent was stripped on a rotary evaporator. The residue was suspended in anhydrous benzene(50ml), and 60mg 18-crown-6 was added with stirring over a period of 15min. To the above solution 0.42g 2 was added, and stirred for 24hrs. Finally condensed, and separated by flash chromatography ($HOAc:CH_2CI_2=1:100$), and 0.32g 4 (Yield 30%) was obtained. Anal. Calc'd for $C_{19}H_{20}N_2O_3Br$: C, 56.17, H, 5.03, N, 6.68, Br, 19.37; Found, C, 56.45, H, 4.99, N, 6.93, Br, 19.76.



Scheme 1 a: $CuCl/O_2$ b: PPh_3/Br_2 c: KOH, 18-crown-6

Its structure was established by IR (Figure 1),ESR (Figure 2), FAB-MS, x-ray and microelemental analysis(see above). The ESR spectrum showed five major lines in the ratio 1:2:3:2:1 expected for coupling with two identical nitrogens.In its IR spectrum,there was an absorption peak at 1364cm^{-1}, which is characteristic of α-nitronyl nitroxide. Due to the isotope effect and its liability of losing one electron, there were peaks at 403,405 besides its parent peak at 404 (M+1) in FAB mass spectrum.

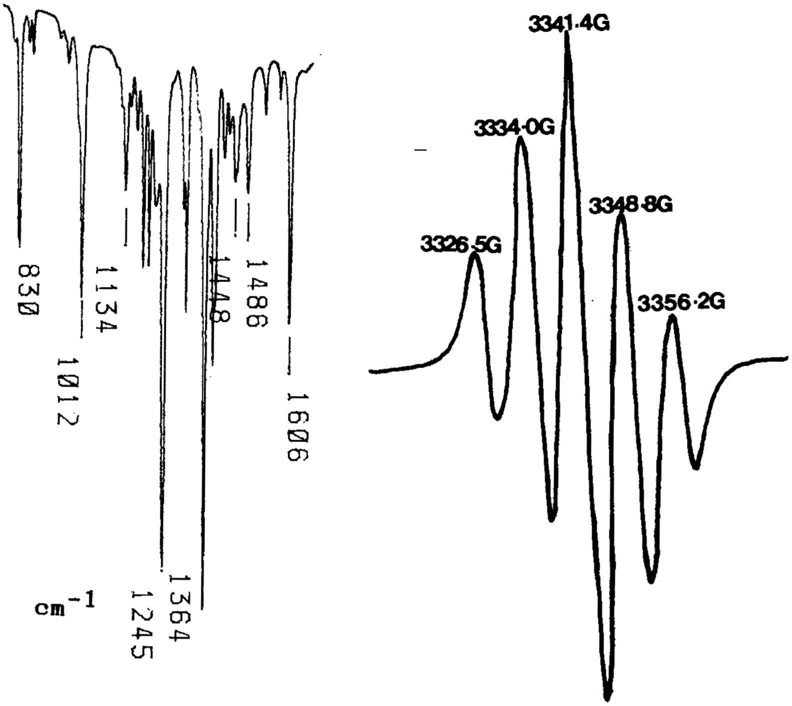


FIGURE 1,2 IR and ESR spectra of compound 4.

The structure was also determined by x-ray diffraction. It belongs to orthorhombic system with a=24.47Å, b=11.04Å,c=7.114Å,V=1931.6Å^3 and space group $P2_12_12_1$. Other detailed information relevant to its structure and packing model will be published elsewhere.

In order to induce topochemical polymerization, we have studied the effects of both radiation and heat. Like BIPO reported by other chemists[9],no change was noted for this monomer 4 by Co^{60} ray radiation up to 60 hours (1.1 Mrad/h). But the monomer can be polymerized by heating in vacuum. The time for complete polymerization varyed from sample to sample.It needed longer time for bigger crystal to polymerize completely. The organic polymer can not be dissolved in usual organic solvents such as aceton, methanol etc.

Similarly, the obtained polymer was characterized with IR (Figure 3) ,ESR(Figure 4). The IR and ESR spectra indicated that the α-nitronyl nitroxide was attached to the polymer backbone.

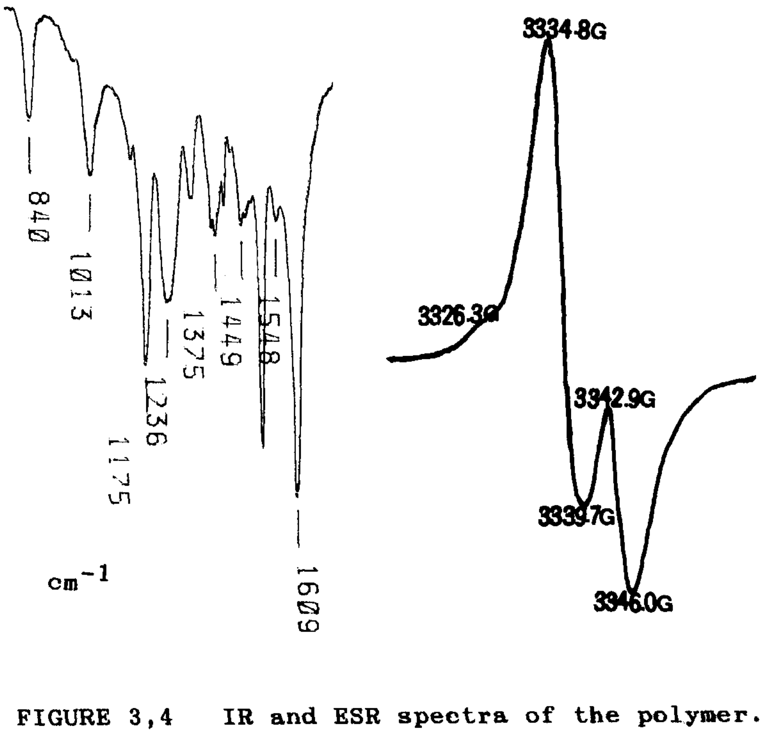


FIGURE 3,4 IR and ESR spectra of the polymer.

MAGNETIC STUDIES

The static magnetic properties were measured on the Extracting Sample Magnetometer. Figure 5 and Figure 6 show the field dependence of magnetization at 1.5K,3K,4K,6K, 10K,the temperature dependence of magnetization at 1T,2T respectively.These results indicate that the polymer with stable organic radical as side group shows no ferromagnetism.

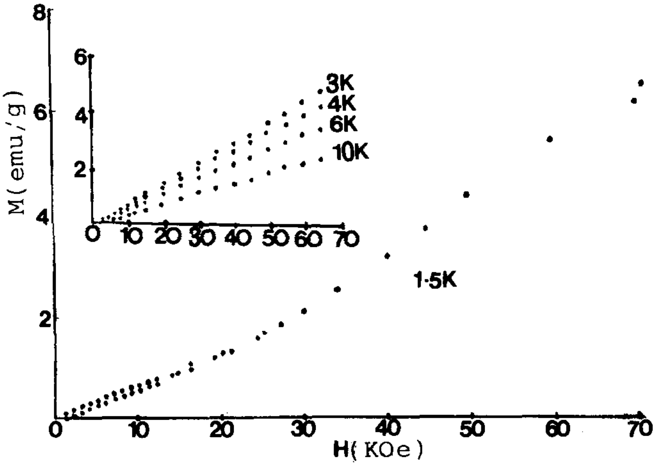


FIGURE 5 Field dependent magnetization plotted at different temperatures.

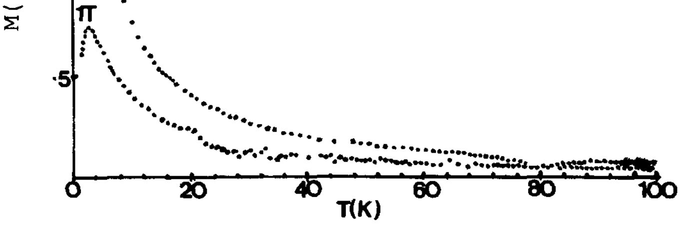


FIGURE 6 Magnetization as a function of temperature at 1T,2T.

The M-H curve at 1.5K has the shape of "S" apparently, which is characteristic of spin glass state. There is always a sharp peak on M-T curve, whose correspoding temperature is about 3K. The maximum magnetic susceptibility x (M/H) of the polymer is about 8 x 10^{-2} emu/g. Therefore, the sharp peak on M-T curve can be regarded as the transition point, at which the paramagnetic state was transformed to spin glass state.

Based on the above facts, we assume that this prepared polymer is in the spin glass state, and further detailed investigation on its structure and magnetic properties is in progress.

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