DNP with Trityl Radicals in Deuterated Polyethylene

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Chemically doping with trityl radicals was performed in fully deuterated polyethylene. The behavior of paramagnetic centers has been investigated by ESR X-band spectrometer. The highest deuteron polarization was 8% at 2.5 T and 1 K with a spin concentration of 3×10^{19} spins/g.

Keywords: Spin; polarization; trityl radical.

1. Introduction

The dynamic nuclear polarization (DNP) is a useful method to enhance the nuclear polarization. The nuclear polarization worked in the early target materials could be satisfactorily applied by the model of the solid effect [1]. It can only be applied to some of the proton target materials where the nuclear (proton) Larmor frequency exceeds the ESR line width significantly. The first of these materials actually used in a particle physics experiment was LMN (lanthanum magnesium nitrate) [2].

If the ESR line width is of the same size or larger than the transition energy between the nuclear Zeeman levels, which is the case in the conventionally doped alcohols and diols, it is not possible to induce only one of the 'forbidden' electron nucleus transitions as it is assumed by the solid effect [1, 3]. Thus a new concept had to be found, which would allow to understand the DNP process also in materials

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with a 'broad' ESR line. This requirement is met by the spin temperature theory [4, 5].

Whereas proton polarization values of more than 90% could be obtained already in the early 1970s [3], deuteron polarization values have been considerably lower, typically 30–50%.

Unlike alcohols and ammonia, polymer materials are solid at room temperature. A big advantage is the fact that the polymer materials can be easily shaped even after the doping procedure.

In former years a polystyrene-based scintillator target has been used, where the TEMPO radicals have been introduced by solution in toluene [6]. A TEMPO doped deuterated polyethylene (CD₂) foil target prepared by the diffusion method has been installed for a 20 MeV fusion experiment [7].

The situation for deuterated compounds has drastically changed with the use of trityl radicals [8]. Trityl doped deuterated butanol targets are used e.g. at the accelerator MAMI in Mainz [9], where deuteron polarization values higher than 85% have been achieved.

The current situation for dynamically polarized deuterated polymer target materials doped with trityl radicals is that in deuterated polystyrene, chemically doped with the trityl radical Finland D36, polarization values up to 60% have been achieved at 5 T with a dilution refrigerator [10].

Based on the high polarization value in trityl radical doped deuterated polystyrene, several samples of CD₂ were prepared for DNP measurements, using the trityl radical Finland D36 as well. First ESR investigations and the deuteron polarization results are reported in this paper.

2. Samples with the Trityl Radical Doping: Preparation and ESR Investigation

Concerning the DNP efficiency, trityl radicals have shown to be the optimal radicals for deuterated alcohol materials [11]. Because of the different solubility in different deuterated materials, the trityl radical Finland D36 has the best performance as a radical for polarized deuterated polymer materials. It has been the first priority to find a solvent which mixes CD₂ and the member of trityl radical family, Finland D36, homogeneously and keeps its stability.

A high deuteron polarization depends on a good coupling between the deuterons and the unpaired electrons. In general, the solvent has to fulfill the conditions of low boiling temperature, quick evaporation and good dissolving property.

Tetralin C₁₀H₁₂ is an organic solvent with a boiling temperature of 206°C and CD₂ powder can be solved in tetralin at a temperature of less than 150°C.

After the CD₂ powder was completely dissolved into tetralin at 150°C in a nitrogen box, Finland D36 was added. The mixture was stirred for several minutes at a temperature of 190°C in order to completely evaporate the solvent tetralin. CD₂ foil sample doped by Finland D36 with a spin concentration 3×10^{19} spins/g

Fig. 1. ESR spectrum of CD_2 sample made by tetralin solvent.

has been investigated by ESR measurements. The ESR line width is shown in Fig. 1, where the peak to peak distance is 0.20 mT. This is similar to that observed in trityl doped deuterated polystyrene [10].

The ESR line width D (FWHM) was calculated to be 0.34 mT.

Fig. 2. Deuteron NMR signal of the positive polarization. The black spectra is the signal and the red one is the fitted line.

Fig. 3. Build-up curve of CD_2 doped with Finland D36.

3. Sample with the Trityl Radical Doping: Polarization Results

The polarization measurements were performed at DNP conditions of 2.5 T/1.0 K. The nuclear magnetic resonance (NMR) signal of maximum positive polarization shown in Fig. 2 was obtained at a microwave frequency of 69.923 GHz.

In order to find out the build-up time, which is the time to reach $(1 - 1/e)$ of the maximum polarization, the build-up curve of the deuteron polarization at optimal microwave frequencies has been measured and is presented in Fig. 3. The bumpy structure in this figure is mainly due to the small amount of CD_2 material (0.1 g) used for the NMR measurements. The highest deuteron polarization was -8% for negative polarization and was only $+3\%$ for positive polarization.

As already measured in irradiated polyethylene samples [12], there is also a large difference between the maximum negative and positive polarization values, which cannot be explained up to now.

4. Conclusions

First trials to dope CD_2 foils with trityl radicals has been done by using tetralin as solvent. As the solubility of CD_2 and Finland D36 inside this solvent depends strongly on the temperature, the high temperature between 150°C and 200°C for dissolving the CD_2 material and evaporating the solvent tetralin afterwards could be problematically.

The radicals can be destroyed and oxygen recombination could be a problem.

In the future, a much more suitable solution method has to be found.

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