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High deuteron polarization in trityl radical doped deuterated polystyrene

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ABSTRACT

Deuterated polystyrene for polarized solid targets has been prepared by chemical doping with the trityl radical 'Finland D36' (AH 110 355 deutero acid form). Thin foils doped with various radical densities have been produced using tetrahydrofuran as solvent. Dynamic nuclear polarization technique has been applied to polarize deuterons in the samples (98%-D) at the temperature range of about 1 K and magnetic fields of 2.5 T and 5.0 T. A maximum deuteron polarization of −61.5% with a build-up time of 100 min has been achieved at 5.0 T and about 500 mK at a radical density of 1.16×10^{19} spins/g.

1. Introduction

High nuclear spin polarizations in polarized solid targets are usually achieved using the dynamic nuclear polarization (DNP) technique that takes advantage of the high thermal polarization of unpaired electrons (about 93% at $B_0 = 2.5$ T and $T = 1$ K compared to 0.25% proton and 0.05% deuteron polarization under the same conditions) by transferring it to the nuclei (protons or deuterons). The polarization transfer is realized by applying a saturating microwave field with a frequency close to the electron Larmor frequency. A comprehensive theoretical treatment of the DNP mechanism can be found in Refs. [1,2].

Unpaired electrons are provided by adding a system of paramagnetic centers to the diamagnetic material. In the case of materials, which are liquid at room temperature (such as butanol, which is one of the standard target materials), this can be done by chemical doping with suited radicals. Another generally applicable method is to induce paramagnetic defects by irradiating the material with ionizing radiation, e.g. an intense electron beam. For an effective DNP process, a number of paramagnetic centers of about 2.0×10^{19} spins/g has been shown to be most suitable.

Since the late 1960s several research groups have put their focus on the development of highly polarizable proton- or deuteron-rich materials for their use as polarized solid targets in particle physics experiments. A comprehensive overview about the achievements made in this field up to the late 1980s together with the particular references can be found in Ref. [3]. More recent overviews are given in Refs. [4,5].

Whereas proton polarization values of more than 90% could be obtained already in the early 1970s [6], deuteron polarization values have been considerably lower, typically 30–50%. This situation has drastically changed with the use of trityl radicals for deuterated compounds [7]. Both of the trityl doped D-butanol and D-propanediol targets used at the accelerator MAMI in Mainz [8] and at the Jefferson National Laboratory [9], respectively, gave deuteron polarization values higher than 85%.

In this paper a new preparation method of D-polystyrene foils doped with the trityl radical 'Finland D36' (AH 110 355 deutero acid form) will be described. The aim of this work was to determine the best radical density for the DNP process in trityl doped D-polystyrene within the temperature and magnetic field range available with respect to our existing DNP equipment.

2. Deuterated polymer target materials

Polarized solid targets which are used for particle physics experiments have to fulfill at least two requirements: (a) a high

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fraction f of polarizable nucleons per molecule and (b) high polarization P at a given magnetic field and temperature. The importance of them may be seen from the figure of merit: $F = \rho \cdot k \cdot f \cdot P^2$, where ρ and k denote the density and the packing factor of the material, respectively. The inverse of F is directly proportional to the data taking time, which is needed in order to achieve a certain statistical accuracy of the particle physics data. From the point of the dilution factor D-polyethylene (CD_2; $f=0.25$) is comparable with D-butanol ($f=0.238$), whereas D-polystyrene (C_8D_8) has a lower dilution factor of 0.143.

Unlike alcohols and ammonia, both polymer materials are solid at room temperature. Therefore the radical doping procedure can be done either by irradiation methods or chemically by diffusion or solution methods using stable radicals at room temperature [10].

A big advantage is the fact that the polymer materials can be easily shaped even after the doping procedure. In addition the packing factor k can be more precisely determined and optimized compared to that of polarizable target materials consisting of tiny beads (alcohols) or chips (ammonia).

The current situation for dynamically polarized deuterated polymer target materials is as follows:

- In D-polyethylene (CD_2) prepared for the DNP process by irradiation, a deuteron polarization of about 35% at 6.5 T with a 1 K ^{4}He-evaporator refrigerator [11] was obtained.
- In D-polystyrene (C_8D_8) chemically doped with the deuterated TEMPO (2,2,6,6-tetramethyl-piperidine-1-oxyl) radical, polarization values up to 40% have been achieved at 2.5 T with a dilution refrigerator [12].

In former years a polystyrene-based scintillator target has been used, where the TEMPO radicals have been introduced by solution in toluene [13]. A TEMPO doped *D*-polyethylene foil target prepared by the diffusion method has been installed for a 20 MeV fusion experiment [14].

3. Preparation of D-polystyrene samples doped with 'Finland D36' and EPR measurements

Based on the pioneering study on polymer material as polarized targets at the Paul Scherrer Institute [15,13], toluene has been used as solvent for D-polystyrene. However, the trityl radical 'Finland D36' (Fig. 1) is insoluble in toluene. Therefore isobutanol which has also a solubility with toluene has been used. Advantageous for the final solidification process is the fact that the boiling points of toluene (383.6 K) and isobutanol (381 K) are roughly the same.

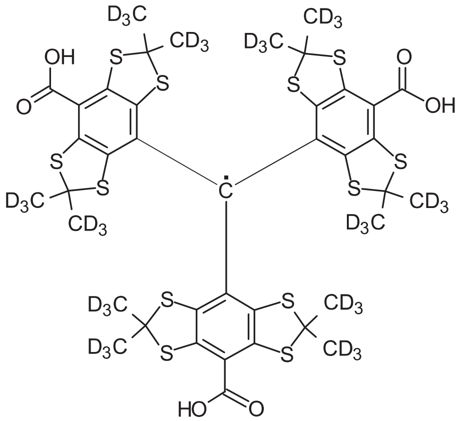

Fig. 1. Molecular structure of the trityl radical 'Finland D36'(AH 110 355 deutero acid form).

At first the preparation procedure was done as follows (Method A):

1. (1) D-polystyrene powder was dissolved in toluene. In another glass 'Finland D36' was dissolved in isobutanol. Both mixtures were stirred until homogeneous and transparent mixtures were obtained.
2. (2) Both solutions were mixed and stirred for 4 h at a temperature around 340 K in order to accelerate the evaporation of both solvents.
3. (3) Finally the mixture (D-polystyrene and 'Finland D36') was poured into a Petri dish and dried at room temperature for 3 h, remaining a transparent thin foil of less than 100 μm thickness.

Electron paramagnetic resonance (EPR) measurements for different foil areas indicate that the 'Finland D36' radical is stable during the entire preparation procedure and show a homogeneous distribution of the radical. However, the sample prepared by this method had given a rather poor reproducibility of the deuteron polarization.

In order to simplify the preparation method tetrahydrofuran (C_4H_8O, THF) was used as solvent. Thanks to its low boiling point (339 K) and its good solubility for both D-polystyrene and 'Finland D36' the preparation scheme became much more simple (Method B):

1. (1) D-polystyrene and 'Finland D36' were dissolved together in THF by stirring until a clear and homogeneous mixture was obtained.
2. (2) The mixture was poured into a Petri dish in a hood in order to evaporate the THF at room temperature.

Fig. 2. Photograph of a D-polysterene foil. The foil thickness increases from 70 μm in the center to 100 μm at the edge.

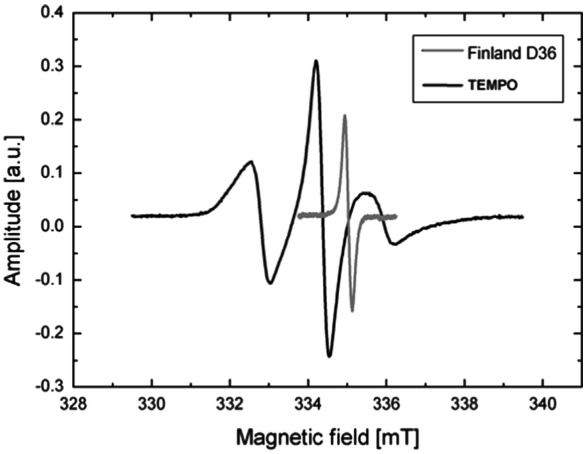

Fig. 3. X-band EPR line of 'Finland D36' in D-polystyrene compared to that of TEMPO in D-polystyrene.