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Polarisation and relaxation characteristics of irradiated polymeric materials at 1 K and at 2.5 T.

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The dynamic polarisation of nuclear spins requires the introduction of paramagnetic centres into potential target materials. A method of choice is the irradiation of such materials, in particular the inorganic materials lithium hydride and ammonia have been used in many nuclear and particle physics experiments with much success. As established as these materials are, a solid target material that can be handled at room temperature and in which the paramagnetic centre remains stable under theses conditions would have many advantages. Initial experiments indicate that the polymeric materials may fulfil these criteria. Polyethylene and polypropylene pellets were irradiated with electrons at various doses and subsequently analysed using Electron Spin Resonance (ESR) spectroscopy. Polarisation values and relaxation times were measured under standard polarised target conditions of 2.5 T and 1 K. The influence of a subsequent heat treatment after irradiation and the resulting change in polarisation characteristics are presented.

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1. Introduction

Polymers have been discussed as candidates for solid state target material for at least the last two decades. Unlike the commonly used alcohols e.g. butanol or inorganics e.g. ammonia, polymer targets have a major advantage in the fact that they can be formed to practically any desired geometry and can thus provide a filling factor close to 1. In addition, the materials are solid at room temperature and handling is unproblematic. The defining point of a good solid state target material is a high polarisation of the proton or deuteron components. The research group at PSI showed dynamic nuclear polarisation (DNP) of protons in thin PE foils and small tubes, chemically doped via diffusion of TEMPO to a spin density of 2×10^{19} spins^{-}/cm^{3}, to values of 70% in a 2.5 T magnetic field at a temperatures below 0.3 K [1], [2]. Ideally one would like to achieve polarisations in polymer materials comparable to the classic materials of over 90%. It has also been proposed that the crystallinity of polymers may in fact be a major factor in obtainable polarisation values, as polarisations seem to be higher in amorphous materials than in crystalline materials at least with regards to chemically doped samples [3]. Kumada et al. [4] showed that for PE doped in the same manner as the PSI materials this was indeed the case. Their ESR studies showed that the chemical dopant TEMPO only diffused into the amorphous regions of the polymer. Whether or not the crystallinity effects the polarisation if the radicals can indeed permeate the crystalline region, as is the case if the materials are irradiated, is still an open question.

2. Polymer sample materials

For the ongoing irradiation studies the focus was placed on two types of long chained polymer molecules: Polyethylene (PE) and polypropylene (PP). The density of both is comparable to that of butanol with a slightly higher dilution factor. PE is a long chain of carbon atoms, each with two associated hydrogen atom substituents (CH_2 monomer - see figure 1). For PP the situation is slightly different: The backbone of the molecule consists of carbon atoms, however next to every polyethylene monomer there is a carbon atom associated with a single hydrogen atom and a CH_3 group (CH_2-CH-CH_3 monomer - see figure 2). The arrangement of the chains can be amorphous, the chains are random and unoriented, crystalline, the chains are folded and packed, or more commonly semi-crystalline in which crystalline structures are dispersed within the amorphous regions.

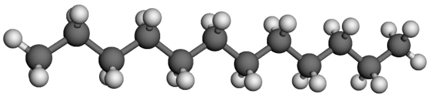


Figure 1: Polyethylene $(CH_2)_n$

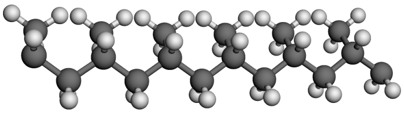


Figure 2: Polypropylene $(CH_2\text{-CH-}CH_3)_m$

Three different types of polyethylene were used.The samples consisted of 1) highly amorphous, low density PE (LDPE) with lots of branching, 2) a low branching, high density PE (HDPE) with a high amount of linearly arranged chains (crystalline) and 3) and linear low density PE (LLDPE), a high branching material interspersed with small crystalline regions. Polypropylene is differentiated by its stereo regularity, the relative orientation of the CH_2 and CH-CH_3 groups. Three isotactic materials of varying chain length were used for which all the substituents are located on the same side of the macromolecular backbone.

3. Classification of samples after irradiation

To achieve high polarisation of nuclei DNP is used to transfer spin polarization from electrons to nuclei. In order for this to be possible electron spins must be introduced into sample materials e.g. by the creation of persisting structural defects by irradiation. In theory hydrogen extraction and chain scissions can occur, however the former is by far more likely in polymer materials. After the irradiation the first step in the analysis of the materials is ESR spectroscopy. The comparison of the spectra of the irradiated material with spectra of a known spin density taken under the same experimental conditions gives access to the spin density of the irradiated material. This essentially tells us how many defects per unit weight were created in the irradiation process. Typical X-band spectra measured at a temperature of 77 K for PE and PP are given in figures 3 and 4.

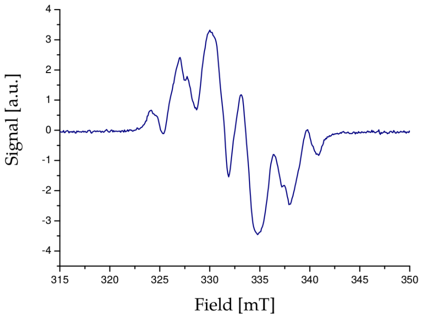


Figure 3: ESR of irradiated polyethylene.

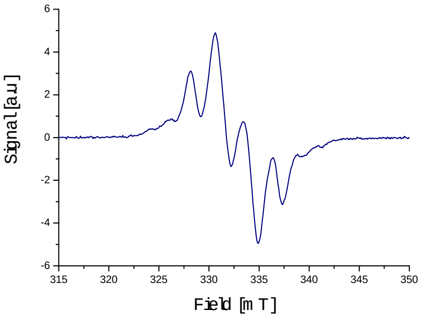
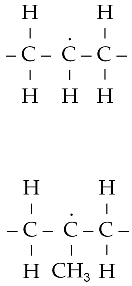


Figure 4: ESR of irradiated polypropylene.



$$-\overset{H}{\underset{H}{C}}-\overset{\cdot}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$$

$$-\overset{H}{\underset{H}{C}}-\overset{\cdot}{\underset{CH_3}{C}}-\overset{H}{\underset{H}{C}}-$$

Figure 5: Primary radicals created by irradiation of PE (top) and PP (bottom).

The ESR spectrum also gives insight into the type of paramagnetic centres that have been be created. Understanding the underlying radical structure can help to optimize the temperature dependent irradiation process with regards to polarisation. An alkyl-type radical (see figure 5) is created in irradiated PE and gives the sextet of the ESR spectrum: The electron is localized on a p-orbital of the single carbon atom and has a hyperfine interaction with the single α- and four surrounding β-protons [5], [6]. On the other hand many structures have been proposed for the radicals resulting from the irradiation of PP, however a general consensus does not seem evident from the literature and major differences have been reported between spectra resulting from different types of irradiation e.g. e^-, γ and UV-sources. The main obstacle in determining the constituents of the spectra is the fact that irradiation of the material is thought to lead to a superposition of radical structures that are primarily obtained by the removal of hydrogen atoms. In polypropylene there are 3 sites from which a hydrogen atom can be removed, each of which would be expected to give an individual and distinct ESR spectrum. A hydrogen atom can be removed from the carbon backbone opposite of the methyl group or from the methylene bridge, as well as from the side-chain methyl itself. The most likely explanation is the dominance of the alkyl-type radical shown in figure 5 with additional structure resulting from the methyl group [7], [8], [9], [10].

4. Preliminary Irradiations at the LINAC1

The electron irradiations in this study have so far been conducted in two consecutive data taking periods. Each of which will be described separately. The LINAC1 of the ELSA facility was used for the initial irradiation. A batch of PP pellets was irradiated in an argon cooled cryostat [11] and subsequently stored in liquid nitrogen. The initial spin density of the material was very close to 5 x 10^{19}e^{-}/g and in the order of magnitude in which one would typically expect DNP to be possible. As illustrated in figure 6 a subsequent heating of the samples in nitrogen at room temperature leads to a significant drop in the spin density. The initial rapid decay of the alkyl-type radical is followed by an almost stable region that lasts for some hours in which the alkyl-type radical is slowly converted into a allyl-type radical [12]. The conversion of the primary radical is evident from the slow increase of a sub-structure in the ESR spectrum, however the contribution of the latter to the spectrum on a whole is minimal and extremely difficult to extract due to the underlying noise. In this regard it is to be expected that any change in polarisation characteristics of the material by heating are related to the primary radical. Two of the characteristics of interest for target materials are the relaxation time and the maximum obtained polarisation values. The change of these characteristics are shown in figures 7 and 8.

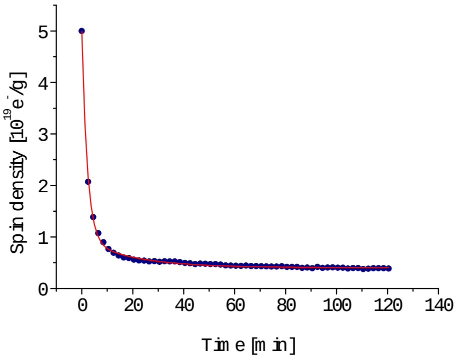


Figure 6: Decay of spin density in irradiated PP caused by heating of sample in nitrogen.

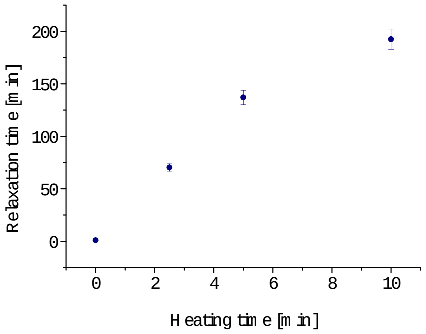


Figure 7: Relaxation times of irradiated PP after heat treatment.

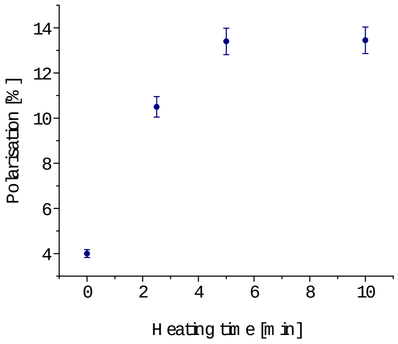


Figure 8: Polarisation of irradiated PP after heat treatment

Samples were analysed at our standard ^{4}He-refrigerator experimental conditions at a temperature of 1 K and a magnetic field of 2.5 T. Samples were heated for 2.5, 5 and 10 min. In these short periods of heating the change of the relaxation times is enormous. The non heated sample has a relaxation time in the region of a minute in comparison to approximately 70 min for the sample heated for only 2.5 min. Additional heating increases the relaxation time further. The non heated sample gave maximum polarisation values of $(4 \pm 0.2)\%$, with additional heating this was increased to $(13.4 \pm 0.6)\%$.

Unfortunately shortly after our introductory efforts the LINAC1 entered a prolonged period of maintenance and it was not possible to conduct any further irradiations of materials at this site: An alternative was needed.

5. Present Irradiations at the LINAC2

In the past all irradiations of target materials in Bonn have taken place at the LINAC1 of the ELSA facility, however at present it is not possible to use this accelerator. Luckily, the second linear accelerator LINAC2 is well maintained and primarily provides electron beams for the Crystal Barrel and BGO groups. Modifications e.g. to the current beamline were needed, however it is now possible to extract the electron beam into the irradiation area. The end energy of LINAC2 is slightly higher than that of LINAC1 with 24 MeV instead of 20 MeV, yet the beam intensity is 20x lower, meaning the irradiation times are significantly longer than in the previous irradiation of the polymeric materials (10 min), yet still not even close to the irradiation times of the non-organic materials such as NH_3 or LiD (>10 h). A typical irradiation time needed to obtain a nominal spin density of $10^{19}e^-/g$ is conveniently in the region of a few hours.

As described in the previous section, a heat treatment of irradiated samples enhances the maximum polarisation values and increases the relaxation times. This positive effect should also be obtained by irradiating the materials above a material dependent specific temperature. In this way the "re-organisation" of the electronic structure is obtained directly during the irradiation. In 20 min the change of the heated sample is more or less completed by the transition of the primary radical into a qausi-stable state. In the case of an irradiation the same (or a similar) radical can be created over a period of a few hours in a much more controlled way. To find the optimal temperature of irradiation a wide range cryostat was used [13],[14]. The cryostat uses a dual regulating system, implementing a slow cycled liquid nitrogen cooled heat exchanger coupled to a closed helium gas system with a fast regulating 1000 W heater. In this way it is possible to irradiate samples at temperatures from 90 K to room temperature with a stability of ± 1 K. The lower beam current of the LINAC2, in comparison to the LINAC1, works in favour of the temperature stability.

At present the work is very preliminary as we have only recently gained access to the facility and a broad outline of the programme will be given. Three different polyethylene samples, differing in density and linearity, and 3 different polypropylene samples, with varying chain length, have been irradiated simultaneously in the above mentioned cryostat. This ensures comparability of the samples: Any differences within a sample batch are thus due to differences in the materials. Irradiations were conducted at temperatures of 140 K, 180 K and 210 K. The injected charge of approximately 3 mC was sufficient to produce radical densities in the order of magnitude necessary for DNP.

As described in the previous section the first analysis of the materials was done with an ESR spectrometer and is summarised in figure 9. It was found that the spin densities of the different types of polyethylene are indistinguishable at the irradiated temperatures and thus the average was taken as a polyethylene batch. The same applies to the polypropylene samples. It is evident that the radical production mechanism in polypropylene is much more effective and the yield of radicals was around 40% higher. Over the analysed temperature range there is a drop in the radical yield to higher temperatures. This is likely mostly due to the temperature dependent recombination process of the primary alkyl radical, as well as the conversion into a secondary radical to a far smaller proportion. As with the heated samples the latter can be seen the in ESR spectrum of the materials, however plays a subordinate role. The alkyl radical is still the dominant radical in all spectra. The analysis of the polarisation values of the irradiated samples at a temperature of 1 K and a magnetic field of 2.5 T is currently in progress.

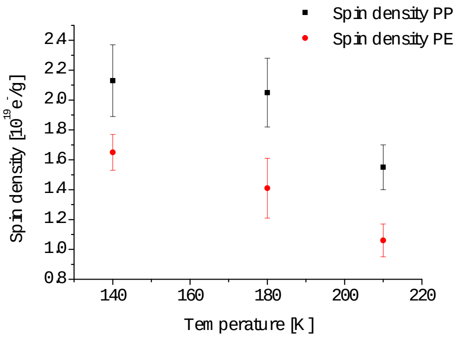


Figure 9: Spin density of PP and PE after irradiation at variuos temperatures.

6. Summary and Outlook

As has been proposed in many papers, polymers can be used in particle physics experiments in which high polarisation values are obtained using DNP. To what extent the polarisation values are adequately high for practical use in such experiments remains to be seen, but previous results from chemically doped samples in the past and current results from the ongoing electron beam irradiations are very promising. The heating of the sample after irradiation has an effect on the relaxation and polarisation characteristics of the samples. Significantly higher values of polarisation are obtained after heating the sample, whilst relaxation rates become longer. The yield of radicals created as paramagnetic centres in PP by irradiation are in the region of 40% higher than in PE at the investigated irradiation temperatures. What influence the irradiation temperature has on the polarisation characteristics is presently being studied: The change of the electronic structure initiated by heating should be obtained directly by irradiation at higher temperatures. Polarisation measurements at very low temperatures are planned for the near future.

References

[1] B. van den Brandt et al. *Dynamic nuclear polarization in thin polymer foils and tubes*, Nuclear Instruments and Methods in Physics Research Section A **356** (1995) 36

[2] B. van den Brandt et al., *Dynamic nuclear polarization in thin polyethylene foils cooled via a superfluid* ^{4}*He film*, Nuclear Instruments and Methods in Physics Research Section A **381** (1996) 219

[3] E. I. Bunyatova, *Free radicals and polarized targets*, Nuclear Instruments and Methods in Physics Research Section A **526** (2004) 22

[4] Kumada et al., *Dynamic nuclear polarization of high- and low-crystallinity polyethylenes*, Nuclear Instruments and Methods in Physics Research Section A **606** (2009) 669

[5] D. Libby and M.G. Ormerod, *Electron spin resonance spectrum of stretched polyethylene*, Journal of Physics and Chemistry of Solids **18** (1961) 316

[6] E.J. Lawton et al., *Paramagnetic-Resonance Studies of Irradiated High-Density Polyethylene. I. Radical Species and the Effect of Environment on Their Behavior*, The Journal of Chemical Physics **33** (1960) 395

[7] H. Fischer and K.-H. Hellwege, *Elektronenspinresonanz-Untersuchungen an bestrahltem Polypropylen* Journal of Polymer Science **56** (1962) 33

[8] L. J. Forrestal and W. G. Hodgson, *Electron spin resonance studies of irradiated polypropylene*, Journal of Polymer Science Part A **2.3** (1964) 1275

[9] M. Iwasaki et al., *Electron spin resonance of trapped free radicals and the photoinduced radical conversion in γ-irradiated isotactic polypropylene*, Journal of Polymer Science Part B: Polymer Letters 5.5 (1967) 423

[10] S. Nara et al., *Configurations of the free radicals in irradiated polypropylene and the relation of their decay reactions to the molecular motion*, Journal of Polymer Science Part A-2: Polymer Physics 8.9 (1970) 929

[11] S. Runkel, *Herstellung und Untersuchung von Ammoniakkristallen als polarisiertes Target für das COMPASS-Experiment*, Univerität Bonn (2011)

[12] T. Fujimura et al., *Conversion of alkyl radicals to allyl radicals in irradiated single crystal mats of polyethylene*, Polymer **19** (1978) 1031

[13] A. Meier, *Entwicklung eines Kryo-Thermostaten hoher Kühlleistung zur Targetpräparation für das COMPASS-Experiment*, Ruhr-Universität Bochum (1997)

[14] S. Reeve, *A Wide Temperature Range Cryostat for Polarised Target Material Preparation*, Univerität Bonn (2011)