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DYNAMIC NUCLEAR POLARIZATION TESTS
IN SOME POLYMERS FOR POLARIZED TARGETS

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INTRODUCTION

In some nuclear and particle physics experiments it is important to have a polarized target material which is solid at room temperature. We have investigated polymer-based materials of the general formula $(CH_2)_n$, because of their high hydrogen concentration and of the low concentration of spin-carrying background nuclei (^{12}C has no nuclear spin, the natural abundance of ^{13}C with spin $I=1/2$ is 1.108 %), and we describe a series of dynamic nuclear polarization (DNP) tests in a variety of samples of these polymers, doped with TEMPO and characterized by electron paramagnetic resonance (EPR).

POLYETHYLENE SAMPLES

The characteristics of the PE samples and the results of the polarization tests are given in Table 1. The samples a and b were prepared with low density PE powder ($d=0.915 \text{ g/cm}^3$). The free stable nitroxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was introduced by thermal diffusion into the PE [1-4].

The samples were investigated by electron paramagnetic resonance. At room temperature the EPR line of TEMPO is a well-resolved triplet as in a viscous liquid, which at 77 K takes a form typical for a radical in a glass-like matrix, and allows the conclusion that the larger part of the radical is in the amorphous part of the polymer. At a TEMPO concentration of 2×10^{19} paramagnetic centres per gram of PE (p.c./g.) one observes a very weak dipolar broadening of the spectral

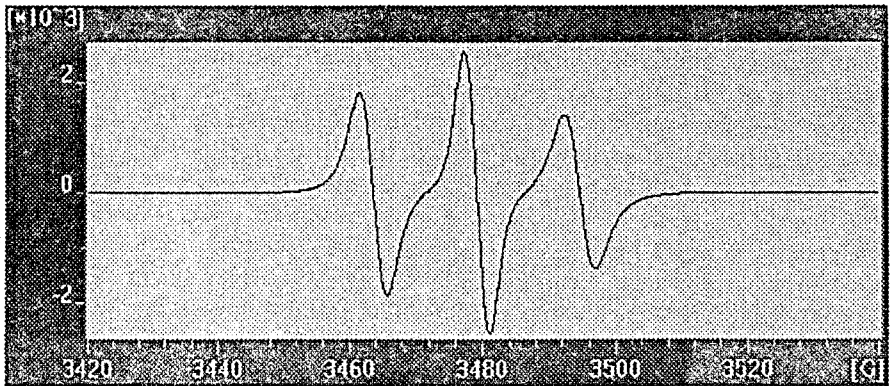


Fig. 1. EPR spectrum of a PE sample with 2×10^{19} p.c./g. at 300 K

lines (Fig. 1), which for a radical concentration of 4×10^{19} p.c./g becomes noticeably larger. The exact local radical concentration in the amorphous part of PE was not determined. However, considering that the major part of the radical is in the amorphous phase of the polymer, which makes up only a part of PE, the local concentration of paramagnetic centres in the amorphous phase of PE is certainly higher than the nominal one.

Table 1. Polarization results and relaxation times in polyethylene (PE) samples at 2.5 T and < 0.3 K

	PE material	radical conc. (p.c./g)	pos. pol. (%)	neg. pol. (%)	$T_{n,1K}$ min.	ref.
a	powder	2×10^{19}	+66	-61	18	3
b	powder	6×10^{19}	+32	-28	0.8	3
c	film 12.5 μ m	2×10^{19}	+48	-47	43	4
d	film 12.5 μ m	5×10^{19}	+26	-21	6	—
e	film 30 μ m	2×10^{19}	+67	—	—	5
f	film 70 μ m	2×10^{19}	+68	-59	8	9
g	microtube	2×10^{19}	+72	-65	8	4

DNP was performed in the standard PSI test set-up [8] in a magnetic field of 2.5 T and at a temperature below 0.3 K. The highest proton polarization in powders was achieved in samples with a TEMPO concentration of 2×10^{19} p.c./g. As the concentration was increased to 4×10^{19} p.c./g, the proton polarization became considerably lower.

PE can be used to make films, tubes, sheets, etc., and in fact we used also commercially produced polyethylene films and microtubes for our tests. Processing of PE into these items results in stretching of the polymer, therefore samples c—g are examples of oriented polymer. In these samples a slightly higher proton polarization could be achieved. It is difficult to draw any certain conclusion about the influence on the DNP processes by the oriented state of PE. This structure differs from the isotropic one in as much that chain sections consist of straightened stressed links of the macromolecule. However, the structure of the oriented polymer, where chemical bonds of the chief-valency chains (CH_2 groups) are predominantly located along one direction, could influence the DNP process.

In terms of polarization, PE powder with TEMPO ranks below such organic substances as alcohols and diols, which allow proton polarizations as high as 98%. Further, polymers are not homogeneous in molecular weight distribution, contain admixtures (catalyzer rests, etc.) and are mostly not homogeneous in phase

composition. However, a target in the form of a thin film or a tube opens up new experimental possibilities [9].

At PSI a Nagoya—Miyazaki—PSI collaboration obtained interesting results in deuterated PE $(\text{CD}_2)_n$ with a deuteration of 98% by weight [7]. $(\text{CH}_2)_n$ and $(\text{CD}_2)_n$ are typical semi-crystalline polymers, part of which are amorphous but consist of the same molecules as the crystalline part. It is not improbable that the whole system cannot be treated as a simple mixture of the crystalline and amorphous substances but as a complex structure of crystalline and amorphous components bound together in a specific manner.

ETHYLENE-PROPYLENE COPOLYMER SAMPLES

The copolymer of ethylene and propylene $(-\text{CH}_2-\text{CH}_2-)_n(-\text{CH}_2-(\text{CH}_3)\text{CH}-)_m$ (EPC) is a fully amorphous polymer, in which the mole concentration of propylene chains in the macromolecule can be as high as 20–60%. With a propylene concentration over 30% by mole, the substance becomes amorphous and rubber-like. Rubbers are a special class of elastic polymers with very flexible chains, whose links rotate around simple bonds rather easily because of thermal motion. The elastic state is similar to the liquid state in some features, e.g., rubbers and liquids have close compressibility factors, but rubbers do not show fluidity under normal conditions because the linkage between their chains is established not only through molecular interaction, as in liquids, but also through chemical bonds. As a result, the polymer has a net-like structure and a good gas permeability, as a thin spatial net is not an obstacle for a gas or vapour.

The amorphous rubber-like EPC can be considered as an interesting homogeneous matrix for the radical TEMPO. Crushed granules of EPC with 60% of $(d = 0.860 \text{ g/cm}^3)$ ethylene were chosen for investigation of the DNP process after doping with TEMPO by diffusion, as in PE (see Table 2).

Table 2. Polarization results and relaxation times of EPC samples at 2.5 T and < 0.3 K

	EPC material	radical conc. (p.c./g.)	pos. pol. (%)	$T_{n,1K}$ min	ref.
i	EPC granules 40% propylene	2×10^{19}	+66	4	—
j	EPC granules 23% propylene	2×10^{19}	+16	—	5

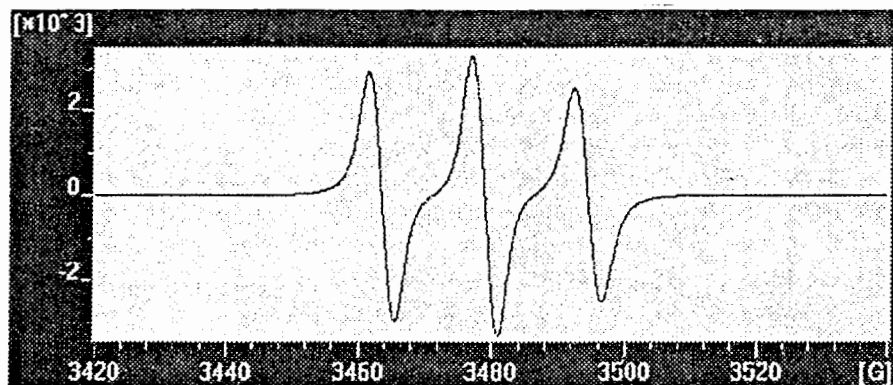


Fig. 2. EPR spectrum of EPC with 2×10^{19} p.c./g at 300 K

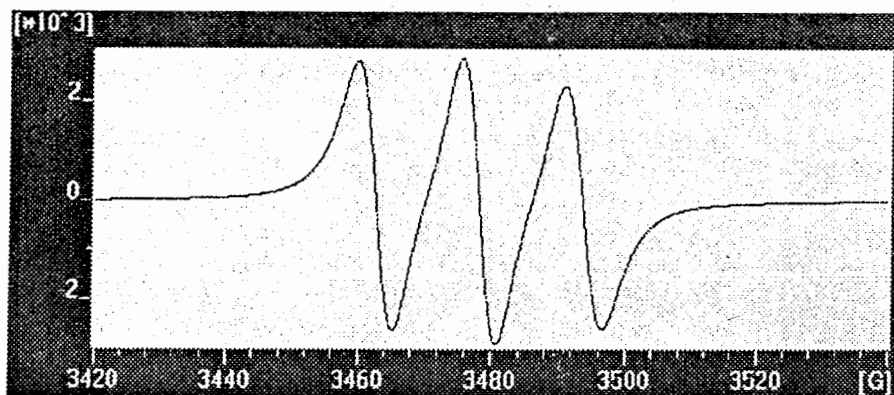


Fig. 3. EPR spectrum of EPC with 8×10^{19} p.c./g at 300 K

The EPR line of TEMPO in the copolymer with a concentration of 2×10^{19} p.c./g is similar to the line of the radical in PE with the same concentration (Fig.2).

A considerable magnetic-dipole broadening was found only at the radical concentration 8×10^{19} p.c./g (Fig.3).

The first experiment to polarize the protons in the EPC sample with a TEMPO concentration 2×10^{19} p.c./g was carried out at 2.5 T and 0.3 K. The proton polarization achieved was 66 %, as high as in our best PE samples (Table 1). However, the spin-lattice relaxation time was shorter than in PE (Table 2).

POLARIZATION TESTS AT 5 TESLA AND 1 KELVIN

In the past a polarized target of lanthanum-manganese nitrate $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ (LMN) has been used as a «polarizing filter» for neutrons in a wide range of energies. Due to the low concentration of background nuclei, organic polymers of the general formula $(\text{CH}_2)_n$ could have considerable advantages over LMN [10]. To test the possible use of PE and EPC as materials for a polarizing filter, these polymers were polarized at 5 T and 1,K the standard conditions for such a filter, and the results are given in Table 3.

Table 3. Polarization results and relaxation times of EPC and PE samples at 5 T and 1 K

	material	radical conc. (p.c./g.)	pos. pol. (%)	neg. pol. (%)	$T_{n,1K}$ min	ref
k	EPC granules	2×10^{19}	+ 19	- 19	0.8	—
l	EPC granules	4×10^{19}	+ 52	- 60	17	—
m	EPC granules	6×10^{19}	+ 44	- 54	15	—
n	EPC granules	2×10^{19}	+ 34	- 28	49	6
p	PE powder	4×10^{19}	+ 15	- 12	25	—
q	PE powder	6×10^{19}	+ 7	- 12	13	—

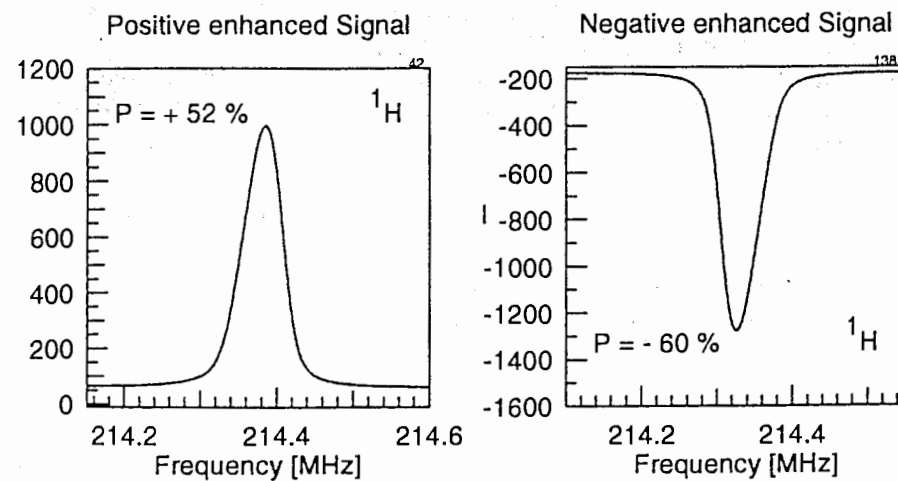


Fig.4. NMR signals at 5 T, 1 K of an EPC sample with 4×10^{19} p.c./g

A proton polarization of 60 % was achieved in the EPC sample with a nominal TEMPO concentration of 4×10^{19} p.c./g (Fig. 4). The polarization in PE samples at 5 T, 1 K was never higher than 20 %. EPC appears to be better polarizable at 5 T and 1 K, possibly because the net-like structure of this fully amorphous polymer is favourable for a homogeneous distribution of radical molecules over the polymer volume. The same open net-like structure suggests a word of caution concerning the long-term stability of the samples, which needs to be investigated further. This work was supported by the International Centre for Science and Technology (Project No.608).

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Исследование методом динамической ядерной поляризации некоторых образцов полимеров для поляризованных мишеней

Представлены экспериментальные результаты динамической поляризации ядер в полиэтилене (ПЭ), сополимере этилена с пропиленом с добавлением стабильного свободного радикала 2,2,6,6-тетраметилпиперидин-1-оксила (ТЕМПО).

Значительная поляризация протонов была достигнута в магнитных полях 2,5 Тл при температуре около 0,3 К и 5 Тл при 1 К.

Работа выполнена в Лаборатории ядерных проблем ОИЯИ.

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Dynamic Nuclear Polarization Tests in Some Polymers for Polarized Targets

The results of dynamic polarization tests in polyethylene (PE) and ethylene-propylene copolymer (EPC), doped with the stable free radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), are presented. Sizable proton polarizations have been achieved in a magnetic field of 2.5 T at a temperature below 0.3 K and of 5T at 1 K.

The investigation has been performed at the Laboratory of Nuclear Problems, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna, 1998