



Dynamic nuclear polarization study of UV-irradiated butanol for hyperpolarized liquid NMR

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ARTICLE INFO

Article history:

Received 1 May 2009

Revised 19 August 2009

Available online 2 September 2009

Keywords:

Dynamic nuclear polarization

Hyperpolarized liquid NMR

UV-photolysis

ABSTRACT

We have carried out a dynamic nuclear polarization (DNP) study of proton spins of UV-irradiated solid butanol containing phenol at 0.1–1%. By the aid of butyl free radicals produced by the photolysis, the butanol sample was dynamically polarized up to the polarization of $1.4 \pm 0.1\%$ at 1.5 K and 1.2 T, which is about 4000 times larger than that at the thermal equilibrium at an ambient temperature. Unlike persistent free radicals such as nitroxy and trityl free radicals commonly used for DNP, the butyl free radicals immediately decay by melting. We propose that free radicals produced by UV-photolysis are applicable to the DNP-enhanced hyperpolarized liquid-state NMR (Ardenkjær-Larsen et al. [6]). The hyperpolarization of the UV-irradiated samples should remain longer than that of the samples having persistent free radicals, because of the absence of the free radicals after the melting in the UV-irradiated samples.

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1. Introduction

It has been established that dynamic nuclear polarization (DNP) results from transferring spin polarization from electrons to nuclei, thereby aligning the nuclear spins to the extent that the electron spins are aligned [1,2]. The DNP technique has received an attention due to its potential application to high-sensitivity NMR; however, it has been used only for solid-state NMR [3,4], because polarization mechanisms, such as the solid effect, the cross effect, and the thermal mixing [2,5] are workable only in solid phase. Since the spectral resolution of the solid-state NMR signals is not so high as that of liquid-state NMR, the application of the technique of the DNP-enhanced solid-state NMR has been limited.

Recently, Ardenkjær-Larsen et al. [6,7] have developed a DNP-enhanced liquid-state NMR method, in which the nuclear spins of a sample are hyperpolarized by DNP in the solid state, and subsequently the sample is rapidly melted and brought into a liquid solution for liquid-state NMR measurement. They thus succeeded in polarizing ^{13}C and ^{15}N in [^{13}C] urea in glycerol containing trityl persistent free radicals at 3.35 T and 1.2 K, and obtained highly resolved liquid-state NMR lines for the first time. The polarizations of ^{13}C ($P_{13\text{C}}$) and ^{15}N ($P_{15\text{N}}$) were 37% and 7.8%, respectively, with their enhancements being 44400 for ^{13}C and 23500 for ^{15}N compared with thermal equilibrium at 9.4 T and ambient temperature. This method does not only enhance liquid-state NMR signals

having high spectral resolution, but also opens new possibility for high-sensitivity *in vivo* MRI.

It is essential to minimize the loss of polarization after the melting for the DNP-enhanced liquid-state NMR and *in vivo* MRI. Nuclear spin-lattice relaxation rates in liquid state are generally proportional to the concentration of paramagnetic species [1]. Therefore, if the free radicals used for the DNP-enhancement were removed after the melting, the hyperpolarization is expected to remain longer. Moreover, free radicals will broaden NMR lines [1], and are potentially toxic to *in vivo* and biological systems [8]. On this account, we should develop a technique to remove the free radicals in order to use the DNP-enhanced liquid-state NMR method to for a wider range of application.

Very recently, McCarney and Han [8] have developed an agarose-based porous media that is covalently spin-labeled with nitroxy persistent radicals. Under ambient temperature at 0.35 T, they extracted hyperpolarized radical-free water having proton polarization $P_H = 5 \times 10^{-3}\%$. The enhancement of the polarization compared with thermal equilibrium was 38 in maximum, being much less than that reported using the low-temperature DNP and subsequent melting ($\sim 10^4$). Thus, there is still great room for improvement in the method to obtain radical-free hyperpolarized liquid samples.

DNP has also been reported for electron-beam (EB) irradiated cryogenic solids, such as lithium hydride [9,10], ammonia [11], polyethylene [12], and butanol [13]. The polarizations of the irradiated samples are comparable to or better than those of the samples containing persistent free radicals. Unlike persistent free radicals, the free radicals produced by the radiolysis immediately decay by melting. In this sense, the DNP technique with

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the EB irradiation could be applicable to the DNP-enhanced liquid NMR; however, the EB irradiation can cause troubles with practical use. For example, samples should be irradiated outside DNP apparatus, because a magnetic field B_0 in a DNP apparatus bends EB. Since the transmittance of a commercial EB for materials is so small that the samples should be pulled out from the sample cells for the irradiation. Moreover, special cares should be taken to control a level of cooling media, such as liquid N_2 and Ar, to minimize the absorption of EB by the media. Because of these difficulties, less attention has been paid to the EB irradiation technique as a commercial application for the DNP-enhanced liquid-state NMR.

Unlike EB, near UV-rays having a wavelength of 200–350 nm are cheaply obtained by UV-lamps or lasers, easily guided by quartz optical fibers, and transparent for quartz windows and such cooling media. If only the free radicals, which can be used for DNP and decay by melting, are cheaply produced by the UV-photolysis instead of the radiolysis, the technique of the UV-photolysis could be applicable to the DNP-enhanced liquid-state NMR. Recently, we succeeded in producing butyl free radicals enough for DNP ($\sim 10^{19}$ spins/cm³) by the UV-photolysis of butanol (C_4H_9OH) containing photo-sensitizer of phenol (C_6H_5OH), and dynamically polarizing up to the polarization $P_H = 1.4 \pm 0.1\%$ at ~ 1.2 T and 1.5 K. We also confirmed that the butyl radicals immediately decay by the melting. In this paper, we will report electron spin resonance (ESR) and DNP results, and discuss the possibility to apply the technique to the DNP-enhanced liquid-state NMR and *in vivo* MRI.

2. Experiment

Fig. 1 shows a schematic view of the UV-irradiation and DNP systems used in this study. *N*-butanol (99%, Kanto Chemical,

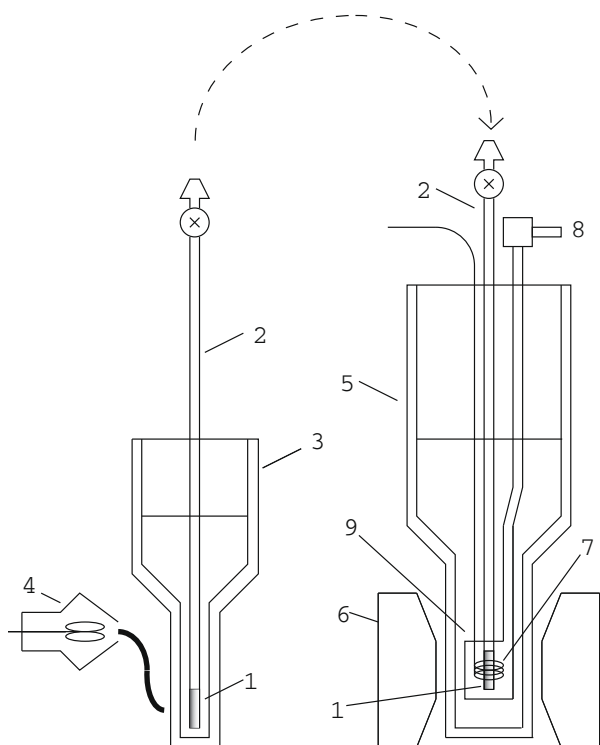


Fig. 1. UV-irradiation system and DNP system. (1) Butanol–phenol sample, (2) sample cell, (3) quartz Dewar filled with liquid N_2 , (4) mercury lamp, (5) glass Dewar filled with liquid He, (6) magnet, (7) NMR coil, (8) frequency-tunable Gunn oscillator, (9) Microwave cavity.

~ 0.1 cm³) containing phenol (99%, Kanto Chemical) by an amount of 0.1–1.0 wt.% was injected into a bottom tip of a quartz sample cell having an inner diameter of 3.2 mm. After freeze deaeration for three times by means of liquid nitrogen, the sample was sealed in the cell together with helium gas for thermal contact, frozen in a quartz Dewar filled with liquid nitrogen. In order to avoid a break of the quartz sample cell induced by a decrease in volume of the butanol–phenol sample by the freezing, we added small pieces of quartz fragments, which induce cracking of the sample into small fragments. The frozen sample was then irradiated with near UV-rays from an ultra-high pressure mercury lamp (Kenko, Super-cure-352S, 250–450 nm, >5000 mW/cm²) for 0.5–2 h. The UV-rays were introduced using an optical fiber, whose end was attached to the outer wall of the quartz Dewar. After the photolysis, the irradiated sample was transferred to a glass Dewar filled with liquid-helium for a DNP experiment.

The DNP system is composed of a glass Dewar for the liquid-helium reservation, a normal conducting magnet for an ESR spectrometer (JEOL, JES TE200), a frequency-tunable Q-band Gunn oscillator (Nakadai, 33–35 GHz, 50 mW), and a continuous wave NMR spectrometer (~ 50 MHz) [14]. Proton polarizations at thermal equilibrium and DNP states were measured at 1.186 T, and at 4.2 and 1.5 K.

We also carried out ESR measurements of the free radical produced by the photolysis. The butanol–phenol sample was settled in a temperature enclosure (Scientific Inst., Model 9650) of the ESR spectrometer (JEOL, JES TE200), and then UV-irradiated at 5 or 77 K through the optical fiber and a window of the ESR cavity. ESR spectra of the UV-irradiated samples were measured at 5–136 K.

Instead of the temperature enclosure, the quartz Dewar used for the DNP measurements was used to determine the concentration of free radicals in the sample used for the DNP measurement. The sample in the quartz Dewar filled with liquid nitrogen was UV-irradiated in a similar manner as that did for the DNP measurement, and then transferred together with the Dewar to the microwave cavity for the ESR measurements at 77 K.

3. Results

3.1. ESR results

Fig. 2 shows ESR spectra of pure butanol and butanol–phenol mixtures irradiated with the UV-rays for 1 h and measured at 77 K. In addition to the lines from an irradiated quartz cell (*) and a manganese marker (Mn), sextet ESR lines (open circles) were observed between 324 and 338 mT in pure butanol. Concentration of the free radicals of the sextet was 10^{16} – 10^{17} spins/cm³, which was much less than that needed for the DNP-enhancement ($\sim 10^{19}$ spins/cm³). These free radicals were more efficiently produced in the butanol–phenol (0.1–1 wt.%) mixtures. On the other hand, although the singlet line (filled circle) was observed, the sextet was not detected in butanol–phenol (20 wt.%).

Fig. 3 shows the concentration of the free radicals as a function of time t of the UV-irradiation. The intensities initially increased steeply, but they showed modest rise after t 10 min. After the UV-rays were irradiated from the other side of the sample at $t \approx 1$ h, the intensities steeply increased again, suggesting that the transmittance of the UV-rays is not enough to produce the free radicals homogeneously. All of the concentrations of the free radicals in the butanol–phenol (0.1, 0.3, and 1.0 wt.%) samples increase in similar manner for each other. The concentration of the free radicals in the sample used for the DNP measurements amounts to $\sim 1 \times 10^{19}$ spins/cm³ after the UV-irradiation for 2 h.

Fig. 4(a–e) shows the ESR spectra of the butanol–phenol (1.0 wt.%) sample irradiated at 77 K and measured at 77–136 K.

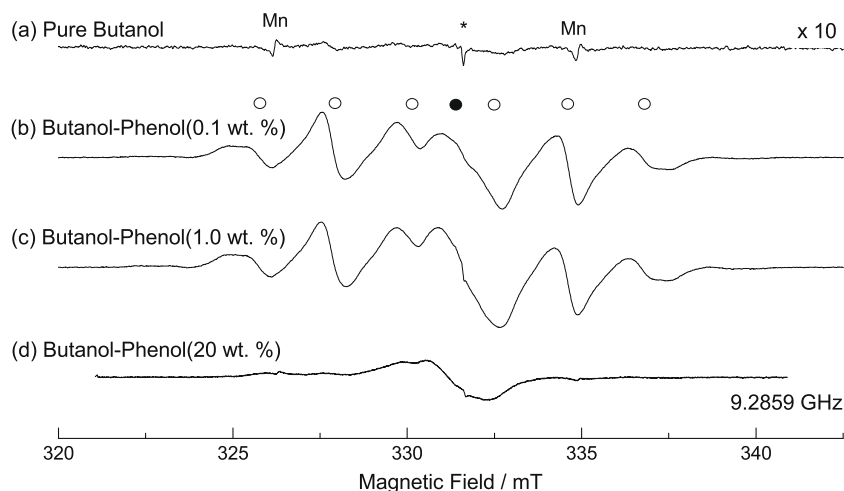


Fig. 2. ESR spectra of butanol–phenol samples irradiated and measured at 77 K. The signals marked by * and Mn are of color centers from UV-irradiated quartz sample cell and a manganic marker, respectively.

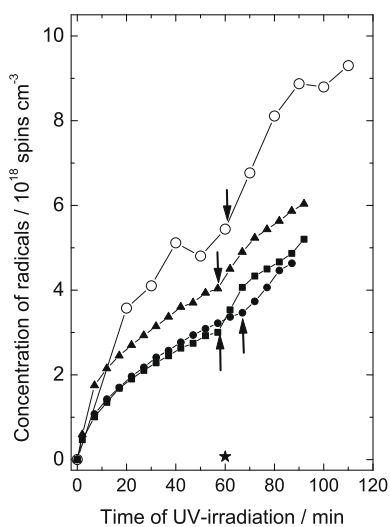


Fig. 3. Concentration of free radicals as a function of time of UV-irradiation. Closed stars, squares, circles, and triangles indicate the butanol–phenol (0, 0.1, 0.3, 1.0 wt.%) samples irradiated in the temperature enclosure at 77 K, respectively. Open circles (○) indicates the butanol–phenol (0.3 wt.%) sample irradiated in the quartz Dewar at 77 K in a similar manner as the sample was irradiated for DNP measurements. Arrow indicates the time when the samples were rotated in order to irradiate the UV-rays on the other side of the sample. It is noted that the concentration has an error of $\sim 30\%$, which can be caused by an ambiguous estimation of the volume of the UV-irradiated sample regions.

As the temperature increases from 77 to 104 K, the intensity of the sextet decreased but that of the singlet increased. Even the singlet decreases with increasing temperature from 104 to 136 K. Neither the singlet nor the sextet was observed at 136 K. Fig. 4(f) shows the spectrum of the sample both irradiated and measured at 5 K. Although the spectral pattern varies as a function of temperature above 77 K, the pattern at 5 K is very similar to that at 77 K.

3.2. DNP results

Fig. 5 shows proton NMR spectra of UV-irradiated butanol–phenol (0.3 wt.%) at the thermal equilibrium (TE) and DNP states. The NMR intensity at the DNP state at 1.186 T and at 4.2 and 1.5 K was

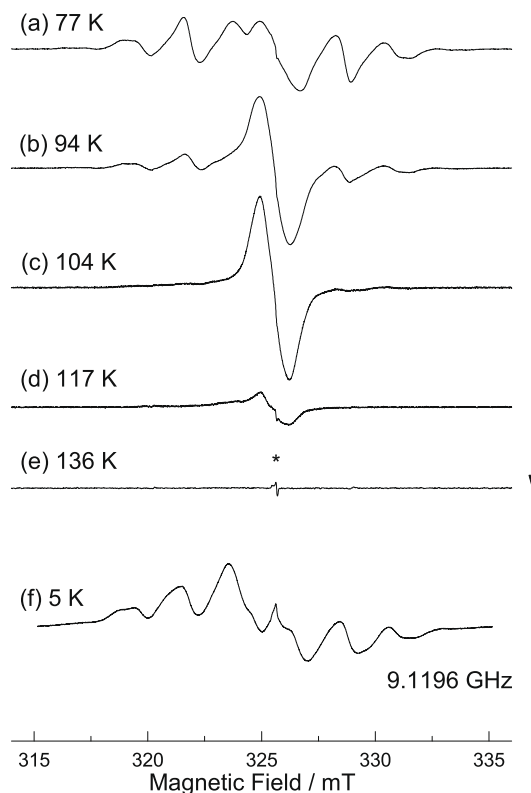


Fig. 4. (a–e) ESR spectra of butanol–phenol (1.0 wt.%) irradiated at 77 K and measured at 77, 94, 104, 117, 136 K, respectively. The sharp singlet marked by * is of the color centers from the UV-irradiated quartz cell. (f) A spectrum of butanol–phenol (1.0 wt.%) irradiated and measured at 5 K.

larger than that at TE at 4.2 K by a factor of 11 ± 1 and 47 ± 3 , respectively. The polarizations P_H were determined by the ratio in the NMR intensity to be $0.32 \pm 0.03\%$ at 4.2 K and $1.4 \pm 0.1\%$ at 1.5 K.

We also measured the DNP-enhancement in butanol containing 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), where $P_H = 89.2\%$ has been reported at 2.5 T and 200 mK [15]. The polarization $P_H = 2.6\%$ was obtained in butanol–TEMPO (2×10^{19} spins/cm³), and $P_H = 0.54\%$ in butanol–TEMPO (1×10^{19} spins/cm³) using our

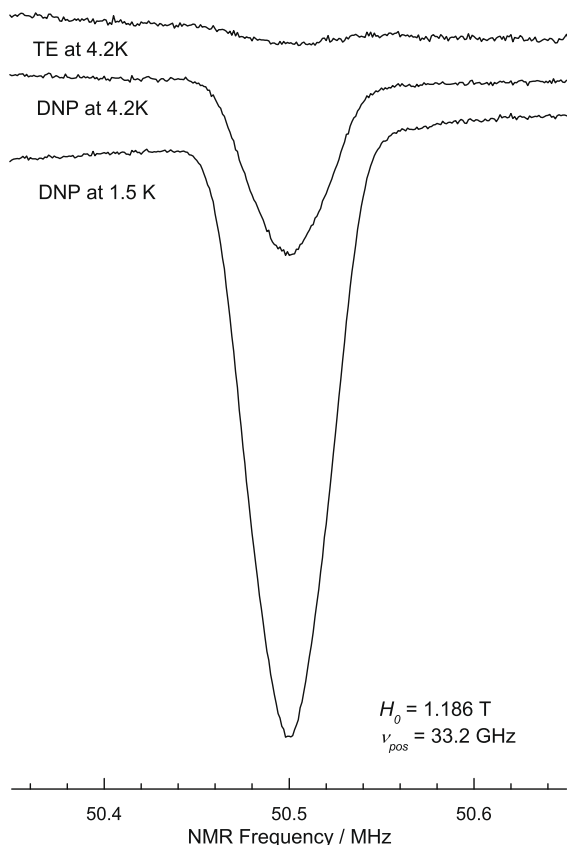


Fig. 5. Proton NMR spectra of UV-irradiated butanol-phenol (0.3 wt.%).

DNP setup at ~ 1.2 T and 1.5 K, being comparable to the P_H value obtained in the UV-irradiated butanol-phenol samples. This result suggests that the polarization of the UV-irradiated sample could be much higher if only higher B_0 and lower T .

Fig. 6 shows a DNP spectrum of the UV-irradiated butanol-phenol sample at 1.186 T and 4.2 K. The maximums of positive and negative polarizations were obtained at $\nu_{\text{pos}} = 33.15$ and $\nu_{\text{neg}} = 33.46$ GHz, respectively. The $\nu_{\text{pos}} - \nu_{\text{neg}}$ value ($= 310$ MHz) was much higher than the double of proton Zeeman frequency ($2g_n\mu_n B_0/h \approx 100$ MHz) but close to the total width of the sextet ESR lines ($\nu_{\text{ESR}} \approx g\mu_B B_{\text{ESR}}/h \approx 250$ MHz).

Fig. 7 shows the enhancement of the proton polarization relative to that at TE at 4.2 K as a function of the UV-irradiation time. The polarization showed the maximum for the irradiation of 1 h for

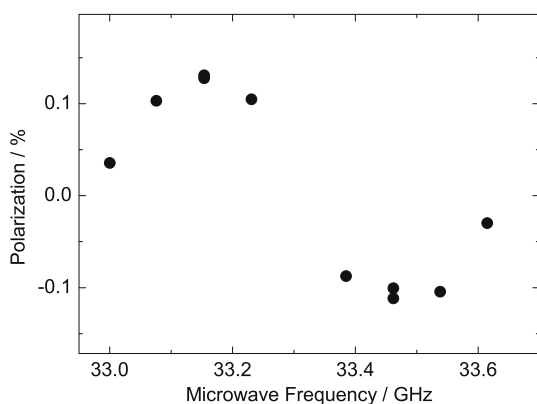


Fig. 6. A DNP spectrum of UV-irradiated butanol-phenol at 4.2 K.

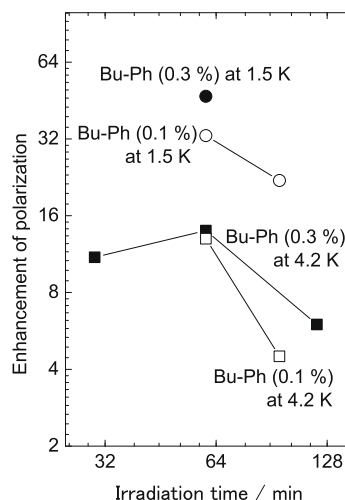


Fig. 7. Enhancement of polarization against TE vs. time of UV-irradiation at 4.2 K.

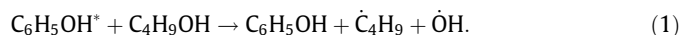
both samples. As shown in Fig. 3, concentration of the free radicals produced by the irradiation for 1 h is less than 10^{19} spins/cm³, whereas it has been reported everywhere that the maximum enhancement of polarization is obtained at the concentration of free radicals of $\sim 2 \times 10^{19}$ spins/cm³. This result may partly due to inhomogeneous distribution of the free radicals in the sample. Local concentration of the free radicals at the surface of the sample irradiated for 2 h may be too high for DNP.

4. Discussions

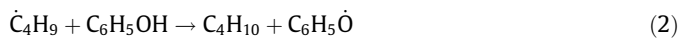
4.1. Free radicals assisting DNP-enhancement

The ESR spectrum in the butanol-phenol (0.1–1.0 wt.%) was composed of sextet lines having a g -value, $g = 2.0029 \pm 0.0010$, and hyperfine coupling constant, $A \approx 2.3$ mT (open circles), and singlet having $g = 2.0037 \pm 0.0010$ (closed circle). Since the ESR intensity of the singlet increased with increasing the concentration of phenol, the singlet is assigned to the phenoxy free radicals, whose isotropic g -value reported ($g_{\text{iso}} = 2.00463$) [16] is very close to that of the singlet. The sextet is most probably butyl free radicals, because the spectral pattern of the sextet is similar to that of the n -butyl free radical produced in γ -ray irradiated n -butylchloride [17,18]. This assignment was also supported by the fact that, instead of the sextet, ESR lines of methyl free radicals having well-known sharp quartet lines separated by 2.3 mT [18], and ethyl free radicals having sharp doublet separated by 2.6 mT and broad anisotropic lines [18] were observed in the UV-irradiated methanol-phenol and ethanol-phenol mixture solids, respectively, (not shown). It is interesting to note that not butyl but butanol free radicals having septet ESR lines are the main product in EB-irradiated solid n -butanol [13,18]. Probably, energy of the UV-rays was not enough to dissociate the C–H bond of butanol.

The lowest excitation energy of phenol ($S_0 \rightarrow \pi\pi^*$, 4.507 eV [19,20]) is close to the energy of $\lambda = 254$ nm line from the mercury lamp (4.88 eV). Although the energy threshold for the $C_4H_9OH + h\nu \rightarrow \dot{C}_4H_9 + \dot{O}H$ reaction has not been reported, the threshold should be close to that of $CH_3OH + h\nu \rightarrow \dot{C}H_3 + \dot{O}H$ (3.952 eV [21]), which is lower than the excitation energy of phenol. Therefore, the butyl free radicals were probably produced by the excitation transfer from photochemically excited phenol ($C_6H_5OH^*$) to butanol,



The butyl free radicals abstract the hydrogen of the hydroxyl group of the neighboring phenols,



Reaction (2) cannot take place if the butyl radicals were immobile and fully surrounded by butanol molecules in the butanol-phenol samples, which is probably the case for butanol-phenol (0.1–1.0 wt.%) at 5–77 K. On the other hand, most of the butyl free radicals can react with a phenol molecule at its neighbor to produce the phenoxy free radicals in butanol-phenol (20 wt.%). The butyl radicals in the butanol-phenol (0.1–1.0 wt.%) diffuse to find the phenol at their neighbor and then react with them to produce the phenoxy free radicals above ~ 90 K. Even the phenoxy free radicals decay probably by radical-radical recombination reaction above ~ 110 K.

We did not obtain any DNP-enhancement in the butanol-phenol (20 wt.%) sample, where only phenoxy free radicals were produced. This result suggests that DNP-enhancement in the butanol-phenol samples results from the transfer of the polarization from the butyl free radicals, not from the phenoxy free radicals. As observed for TEMPO in solid butanol, ESR intensity of the butyl radicals increased in proportional to the square root of the microwave power up to $10 \mu\text{W}$ at 5 K. On the other hand, the intensity of the phenoxy free radicals completely saturated above $1 \mu\text{W}$ (not shown). This result indicates that electron spin relaxation of the phenoxy free radicals is much slower than that of butyl and TEMPO free radicals. We therefore speculate that, because of such slow spin relaxation, the phenoxy free radicals cannot absorb the microwave for DNP effectively.

4.2. DNP mechanism and possibility for higher polarization

As observed in the butanol-TEMPO samples [13,15,22], the polarization of the UV-irradiated butanol-phenol samples will increase with increasing B_0 and decreasing T . The ESR spectrum of the butyl radical was broadened and split into the sextet by inhomogeneous interactions such as anisotropy of g -value and hyperfine interaction. The total width of the butyl radicals (≈ 250 MHz) is larger than $2g_n\mu_n B_0/h$ (≈ 100 MHz). Therefore, the DNP of the UV-irradiated butanol-phenol probably took place by the cross effect rather than the solid effect and thermal mixing. Based on the theory of the cross effect [2,5], the highest nuclear polarization is obtained when ESR linewidth of free radicals for DNP is equal to the double of the nuclear Zeeman frequency. In such condition, the relation, $\nu_{\text{pos}} - \nu_{\text{neg}} \approx 2g_n\mu_n B_0/h$, is satisfied in DNP spectra, but $\nu_{\text{pos}} - \nu_{\text{neg}}$ ($= 310$ MHz) is larger than $2g_n\mu_n B_0/h$ by a factor of 3 in the UV-irradiated butanol-phenol sample at 1.2 T (See Fig. 6). This result indicates that $B_0 = 1.2$ T is too small to obtain higher P_H . Generally, the polarization P_H increases with increasing B_0 , but decreases when B_0 exceeds 2.5–5 T [13,22]. The decrease is due to broadening of the ESR linewidth due to $\Delta g/g$ at higher B_0 . The $\Delta g/g$ value for the butyl free radicals ($< 1 \times 10^{-3}$) determined by the analysis of the ESR lineshape is smaller than that of the free radicals generally used for DNP-enhancements, such as the hydroxyalkyl (1.25×10^{-3}), nitroxyl (3.85×10^{-3}), porphyrin (4.01×10^{-3}) and Cr(V) (6×10^{-3}) free radicals [13,22]. Therefore, the polarization P_H in the UV-irradiated butanol-phenol samples is expected to increase with increasing B_0 up to higher B_0 .

4.3. Requirements of UV-irradiated samples for DNP and DNP-enhanced liquid-state NMR and *in vivo* MRI

Near UV-rays dissociate various kinds of molecules into fragments of free radicals. However, not only magnetic properties of

the free radicals themselves, such as ESR parameters and electron spin relaxation rate, but also the following requirements should be satisfied in order to use the photochemically produced free radical for DNP and the DNP-enhanced liquid-state NMR, and *in vivo* MRI.

First, cross sections for photodissociation should be large enough to produce free radicals for DNP within a decent timescale. As shown in Fig. 2(a), rate for the generation of the radicals in pure butanol is so slow that it would take 100–1000 h to reach the concentration required for DNP. We overcame the difficulty by adding the photo-sensitizer of phenol.

Second, yield of by-product free radicals produced by UV-photolysis should be minimized. Generally, more than two kinds of free radicals are produced by photolysis. Even if one kind of radical can be used for DNP, the other kind of free radical cannot be used. They only help nuclear spin relaxation to decrease polarization. We should select the reaction system, in which the by-product free radicals do not decrease the polarization much. We added phenol to the butanol sample as small as possible in order to minimize the yield of phenoxy free radicals. OH radicals, which are by-product free radical of Reaction (1), have not been observed by ESR. They may react with other butanol or phenol molecules to produce other kinds of free radicals, which more or less decrease the polarization.

Third, for the *in vivo* MRI use, the samples should be less toxic. Since both butanol ($\text{LD}_{50} = 2680$ mg/kg in mice) and phenol ($\text{LD}_{50} = 270$ mg/kg in mice) are toxic, the butanol-phenol samples used in this study are not adequate for *in vivo* MRI. However, if only less toxic solvent and solute were found, the DNP technique with photochemically generated free radicals would be applicable to the DNP-enhanced MRI.

Finally, we mention two possible improvements of the DNP apparatus. One is to skip the sample transfer between the UV-irradiation and DNP measurement. In this study, the sample in the quartz Dewar was irradiated and then transferred to the DNP apparatus. However, if only UV-rays from a laser such as fourth harmonic Nd:YAG laser (266 nm) were introduced into the butanol-phenol sample in the DNP apparatus through an optical fiber, the free radicals can be produced much more quickly, and then the UV-irradiated sample can be polarized without the transfer of the sample. The other is the improvement of the transmittance of the sample. Fig. 3 shows that the transmittance of the UV-rays through the sample was not enough to produce the free radicals homogeneously. Since the concentrations of the free radicals in the butanol-phenol (0.1–1 wt.%) increased in a similar manner, the transmittance would not be determined by photo-absorption with the phenol. We speculate that the pieces of the quartz fragments and the cracks of the sample produced by the quartz fragments would scatter the UV-rays to decrease the transmittance. Highly transparent sample in a stalwart quartz cell, which withstands the volume change of the sample, may be required to polarize larger volume of samples using the UV-irradiation technique.

5. Conclusion

We achieved the maximum proton polarization of $1.4 \pm 0.1\%$ for UV-irradiated butanol-phenol (0.3 wt.%) at 1.2 T and 1.5 K using a technique of DNP. The free radicals which mediated DNP disappeared by heating the sample above 120 K. We propose that this technique could be applicable to dynamically polarized liquid NMR, in which the free radicals remained in the liquid sample promote depolarization of the nuclear spins.

We also point out that this technique could be applied to *in vivo* MRI, if we found dynamically polarized samples composed of a less toxic photo-sensitizer and solvent. Since both butanol and phenol are toxic, the butanol-phenol sample itself cannot be applied for

variety of biological systems. However, the technique of the UV-irradiation should be a promising technique if such an enhancement of nuclear polarization is obtained for a less toxic photo-sensitizer and solvent.

Acknowledgments

We express our gratitude to Dr. B. van den Brandt and Dr. P. Haulte in Paul Sherrer Institute, and Prof. N. Horikawa in Chubu University for fruitful comments and discussion. We thank to Dr. T. Ichikawa in Hokkaido University for suggestions on handling of cryocrystals, and analysis of ESR spectra. We also thank Dr. M. Saeki in Japan Atomic Energy Agency (JAEA) for the analysis of photochemical reactions, and Dr. Y. Kurosaki in JAEA for reading this paper. This research was supported by a grant from the sprouting research in JAEA.

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