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High Resolution Solid State NMR in Liquids 3.[1] ^{1}H NMR Study of Organic Nano-Particles

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High resolution ^{1}H NMR spectra of terephthalic acid (TPA) ultrafine particles (UFP's) were obtained by means of motional narrowing caused by Brownian motion of UFP's in a liquid phase of CCl_4. In the case of dispersing condition of UFP's, highly resolved signals from benzoic protons were obtained at 6.85, 6.95, 7.08, 7.25, 7.50 and 7.65 ppm with respect to tetramethylsilane (TMS), even though only a signal at 8.15 ppm was obtained from moleculary dispersed TPA in acetone. Particle size was obtained to be ca. 15 nm by a dynamic laser scattering method.

In recent years solid state NMR studies have been extensively reported in various fields of science.[2] This trend clearly shows that solid-state NMR has become a quite important technique not only as a subject of NMR science but also as a powerful tool for analytical techniques. NMR spectral lines of solid-state samples are, in general, quite broad due to various reasons such as a dipole-dipole interaction, anisotropy of chemical shift, etc. Therefore, it is inevitable to reduce the broad line width in order to get useful NMR parameters such as precise position of chemical shifts, multiplet of lines and so forth. There have been basically two conventional techniques for obtaining high resolution solid-state NMR spectra, namely, magic angle sample-spinning (MAS NMR) with decoupling of dipole-dipole interaction and that based on multiple-pulse sequences.[3] However, satisfactory resolution has not yet been obtained by the use of these techniques for protons. It is still quite difficult to achieve high resolution NMR for protons in solids if a proton nucleus is surrounded by abundant homogeneous proton nuclei having large magnetic dipoles. In such a case the decoupling technique which is effective for dilute spin systems can not be used, since both magnetic moments of the targeting proton and the surrounding protons are simultaneously excited by decoupling irradiation. High resolution solid state ^{1}H NMR is thus one of the challenging goals for current NMR science.

Rapid and random motions of nuclei in a solid suppress these broadening effects,[4] which is well known as motional narrowing. The present authors have demonstrated that Brownian motion of nanometer-sized particles in a liquid phase provides well-resolved high resolution NMR spectra for solid state samples, which we named "UFP (ultrafine particle)-NMR" [5] in the first paper of this series. One of the advantages of the UFP-NMR method is *in situ* information concerning solid surfaces without the need of a high vacuum condition as required in most other techniques.[6] Another merit of UFP-NMR is that the motional narrowing can be expected to provide high resolution spectra irrespective of their origin of the broadening. We report here that UFP-NMR is applicable to a high resolution magnetic resonance of nuclei surrounded by

homogeneous abundant spins in solids, namely, high resolution solid-state ^1H NMR. High resolution solid-state ^1H NMR from UFP's of terephthalic acid (TPA) dispersed in carbon tetrachloride (CCl_4) are demonstrated. TPA-UFP was chosen as a test material for UFP ^1H NMR because TPA is chemically stable against thermal treatments such as a sublimation process. Low solubility of TPA to conventional solvents for ^1H NMR measurements is also important to stabilize a UFP state. Preparation of organic UFP's is itself a new challenge, since few studies have been reported as for an effective technique to prepare organic UFP's. We also report here a novel method to prepare dispersions of organic nanometer-sized particles with a diameter of ca. 10 nm. Well resolved signals were obtained from benzoic protons of TPA when TPA-UFP's were dispersed in CCl_4. The results from UFP-NMR method are discussed comparing with those from solid state ^1H NMR via the CRAMPS method and a conventional liquid state NMR.

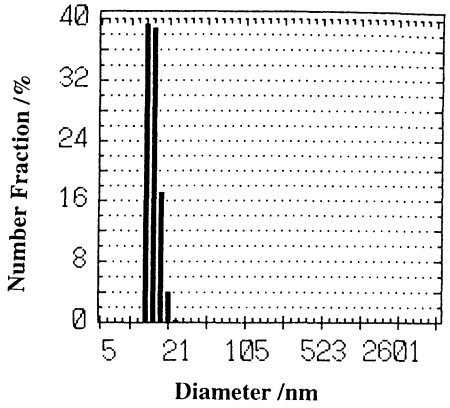

Fig. 1. The particle size distribution of TPA-UFP (4.0 nm thickness)/ acetone-D6/ CCl_4 obtained by DLS measurement.

Guaranteed grade of TPA was purified twice by sublimation in a vacuum condition being held at 270 °C. Dispersing liquid CCl_4 was purified by 4A molecular sieves and active carbon powder. Basic idea to obtain TPA-UFP dispersion is based on an island like deposition on a cold matrix by the vacuum evaporation method. CCl_4 was chosen as a dispersing media because solubility of TPA to CCl_4 is extremely low. Surfactant is not suitable to disperse the UFP because of the following reasons. Surfactant molecules have generally a large molecular weight and a molecular length, which is disadvantageous for obtaining small UFP's. Moreover, proton signals of surfactants may disturb the signals of UFP's. Deutrated acetone (acetone-D6) or deuterated methanol (methanol-D4) was chosen as a dispersing reagent. The detailed preparation method will be described in the following report. Briefly, bulk TPA was settled in an aluminum coated heater. The glass chamber was once evacuated less than $1.0X10^{-6}$ Torr by a molecular turbo pump. The wall of the chamber was then cooled by liquid nitrogen in order to deposit a cold matrix of CCl_4. Evaporation of CCl_4 was continued for 90 s, which was followed by sublimation of TPA on the CCl_4 cold matrix. The amount of TPA deposited was controlled to be ca. 4.0 nm monitoring with a quartz film-thickness monitor. Island like deposition of TPA was confirmed through TEM observations to be achieved with above conditions. After the sublimation of TPA, acetone-D6 or methanol-D4 was evaporated on TPA particles for less than one second. These three deposition steps of CCl_4, TPA and dispersing reagent were repeated nine times in this order. Liquid CCl_4 was then added on the cold matrix to prepare the concentration of acetone-D6 or methanol-D4 being 1 vol% of total volume of the dispersion. Finally, matrix was melted under ultrasonic wave. Although the dispersion was transparent, Tyndal scattering was clearly observed by irradiation of a He-Ne laser. Dynamic laser scattering (DLS) measurements were carried out for obtaining size distributions of UFP.

^1H NMR measurements on dispersion and liquid samples were carried out on a conventional FT NMR spectrometer, JEOL GX400 using a probe for irradiation frequency of 399.8 MHz. Colloidal or liquid samples were sealed into a conventional 5-mm sample tube with 17 Hz sample spinning rate.

The CRAMPS NMR spectra were recorded on a CMX-400 type FT NMR spectrometer (Chemagnetics Ltd.) with a CRAMPS probe with BR-24 pulse-sequence.

Figure 1 shows a number distribution of TPA-UFP/acetone-D6/ CCl_4 obtained by DLS measurements. Small particles with a diameter ca.15 nm are obtained in both systems. However, the Tyndal scattering was lost and no signal was obtained by DLS when the evaporation of TPA was continued up to 230 nm in thickness in the preparation process. This fact suggests that there is a critical thickness such as percolation limit for obtaining UFP's above which island-like deposits grow to films.

Figure 2 shows ^1H NMR spectra from benzoic protons of TPA in various state of TPA after 500 accumulation times. The colloidal dispersion of TPA-UFP/ acetone-D6/ CCl_4 provides six peaks, which are located at 6.85 ppm, 6.95 ppm, 7.08 ppm, 7.25 ppm, 7.50 ppm and 7.65 ppm as seen in Fig. 2(a). The full widths at half maximum (FWHM) of six peaks are of the order of 0.1 ppm, i.e. 40 Hz. The same six signals with an additional peak positioned at 8.15 ppm are appeared in the case of TPA-UFP/ methanol-D4/ CCl_4 system (Fig. 2(b)). The original signal from benzoic protons of TPA dissolved in acetone-D6 is referenced in Fig. 2(e). Comparing with Fig. 2(e), the signal of 8.15 ppm in Fig. 2(b) is identified with that from moleculary dissolved TPA. Because of rather higher solubility of TPA in methanol than in acetone a small amount of TPA is supposed to dissolve into liquid phase in the TPA-UFP/ methanol/ CCl_4 system. In all above spectra carboxyl protons were not observed.

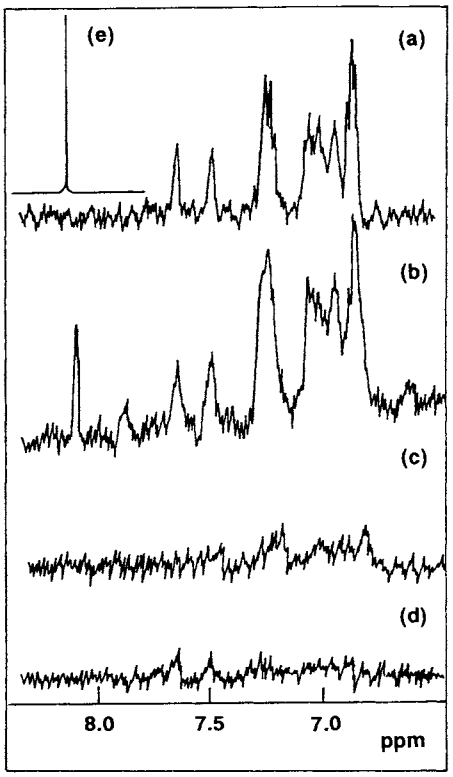

Fig. 2. ^1H NMR spectra of benzoic protons of TPA by a conventional NMR spectrometer. (a) TPA-UFP (4.0 nm thickness)/ acetone-D6/ CCl_4, (b) TPA-UFP (4.0 nm thickness)/ methanol-D4/ CCl_4, (c) TPA-UFP (4.0 nm thickness)/ CCl_4, (d) TPA-UFP (230.0 nm thickness)/ acetone-D6/ CCl_4 and (e) moleculary dispersed TPA in acetone-D6.

The signals from the TPA-UFP/ dispersing reagent/ CCl_4 systems (Figs. 2(a) and (b)) were significantly diminished both when the dispersing reagents were not used on the preparation process and when TPA was evaporated over 200 nm thickness. Figs. 2(c) and (d) show ^1H NMR spectra from a TPA-UFP (4 nm thickness) / CCl_4 system and a TPA-UFP (230 nm thickness)/ acetone-D6/ CCl_4 system, respectively. The signals observed in the UFP dispersions were dramatically weakened in both spectra being consistent with the results from DLS measurements. Furthermore, no signal was observed neither from TPA saturated acetone-D6 diluted with 100 times nor even with 2.5 times volumes of CCl_4. These results strongly suggest that the six signals observed in Figs. 2(a) and (b) are originated from the dispersing TPA-UFP's in CCl_4.

In order to confirm that the signals are definitely from TPA-UFP's following procedures were employed. Firstly, dried powder from TPA-UFP/ acetone-D6/ CCl_4 was dissolved into acetone-D6. Intensities of the six signals ranging from 6.8 to 7.8 ppm were decreased, and a new peak indicating moleculary dissolving TPA were alternatively developed at 8.15 ppm. To completely dissolve TPA-UFP's, the sample, TPA-UFP/ acetone-D6/ CCl_4 dispersion was once evacuated to remove solvents being followed by a sublimation process at 290 °C,

and then the powder obtained was dissolved again in acetone-D6. Whole processes were carried out in the same NMR sample tube. There can be observed only moleculary dissolving signal of TPA at 8.15 ppm after this resublimation treatment. Coincidentally, the strong light scattering by irradiation of He-Ne laser was drastically extinguished in the sublimation treated sample.These observations strongly support that the six peaks found in Figs. 2(a) and (b) are due to TPA-UFP's.

Even by the CRAMPS method, a high resolution signal is in general difficult to achieve especially for benzoic protons. Figure 3 shows the solid state ^{1}H NMR spectrum of bulk TPA via CRAMPS. Note that the signal is represented on a reduced scale of chemical shift. The broad peak observed is centered at 7.3 ppm, which is ranged over the same region with that of dispersed UFP. However, the width (FWHM) of the peak reaches 1.95 ppm, i.e. 0.78 kHz and fine structures are hardly observed.

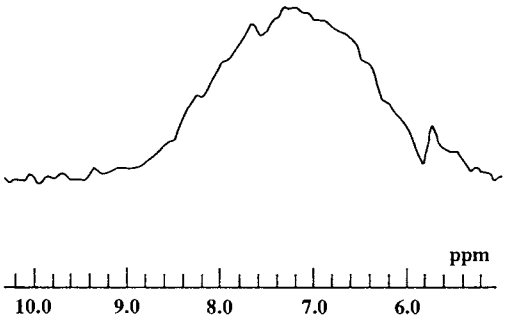

Fig. 3. Solid state ^{1}H NMR spectra of bulk TPA via CRAMPS method with 118 times of accumulation. L-alanine was used as an external referential standard of chemical shift, namely, at 1.3 ppm lower field from TMS.[8]

Chemical shifts of benzoic protons are varied from 6.85 ppm to 8.15 ppm according to the state of TPA, i.e. UFP, solid state and moleculary dispersion. In moleculary dispersing state all four benzoic protons are equivalent providing single NMR peak, 8.15 ppm because of high speed rotation of the carboxyl groups. In the solid state carboxyl groups of TPA were reported to be in a trans conformation according to crystallographic data.[7] Benzoic protons of TPA are not already equivalent in this state. Furthermore, two types of crystal forms, both of which are based on triclinic crystal, are known.[7] This polymorphs of solid TPA can be one cause to explain these six signals of TPA-UFP. Another explanation for this variety in the chemical shift is based on the trait of UFP. Since one-third of molecules must be exposed on the surface of the TPA UFP with a diameter of 15 nm, they may provide more than one type of signal for each proton.

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