FOCUS REVIEW

Structural analysis of polymers via solid-state dynamic nuclear polarization (DNP)-NMR

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Abstract

Solid-state NMR is one of the most powerful analytical methods for the structural characterization and dynamics of polymers. Owing to its intrinsically low signal sensitivity, however, analysis of trace chemical species supported on polymers remains challenging. Solid-state NMR with dynamic nuclear polarization (DNP-NMR) has recently attracted attention as a highly sensitive NMR measurement method for analyzing polymers. We recently investigated DNP-NMR for insoluble polymers, particularly cross-linked polymers, engineering plastics, and polymer-supported catalysts, and achieved high NMR signal sensitivity at a routinely accessible level. In this focus review, we present case studies on DNP-NMR measurements for a wide range of polymers.

Introduction

Understanding molecular-scale as well as higher-order polymer structures is key to the rational development of polymeric materials. Various methods are available for the structural analysis of polymers, including FT-IR [1], Raman spectroscopy [1], mass spectrometry [2], X-ray scattering [3], neutron scattering [4], solution NMR [5], and solid-state NMR [6]. Among them, solid-state NMR is a highly useful analytical method for characterizing the molecular structure and dynamics of polymers in a nondestructive manner. While analysis of the ratio of amorphous/crystalline phases and their dynamics via time-domain NMR utilizes the observation of ^{1}H nuclei with high sensitivity, making high-throughput measurement feasible, high-field NMR targets mainly nuclei with a low natural abundance and a low gyromagnetic ratio (γ), such as ^{13}C nuclei, whose NMR signal sensitivity is inherently insufficient for routine analysis. Therefore, various methods, such as the magic angle spinning (MAS) and the cross-polarization (CP) methods, have been developed to

enhance NMR signal sensitivity and resolution. Solid-state NMR with dynamic nuclear polarization (DNP) (Fig. 1) has recently attracted attention as a highly sensitive approach for analyzing solid-state materials [7]. In DNP-NMR, microwave irradiation in the presence of an appropriate radical compound (polarizing agent) induces spin polarization transfer from electron spins to nuclei. Although the principle of DNP itself was developed by Overhauser in the 1950s [8], practical DNP measurements were recently achieved by Griffin and coworkers, who utilized a gyrotron to realize DNP under high magnetic field conditions. Notably, studies on the structural analysis of polymers via prototypical DNP-NMR were pioneered by Schaefer et al. in the 1990s [9, 10]. Various radicals have been investigated to achieve efficient DNP enhancement. For example, Griffin et al. reported DNP-NMR of polystyrene (PS) with BDPA as a polarizing agent under high-field conditions [11] and Horii et al. demonstrated the utility of nitroxyl radicals for the analysis of poly(methyl methacrylate) [12]. Recent works have focused mainly on the cross-effect with a biradical compound (Fig. 2): a nitroxyl radical at an appropriate distance was found to be useful in the 2000s, and various materials were evaluated via DNP-NMR using this approach [7, 13–15]. Compared with inorganic materials that possess large specific surface areas such as silica [16], few studies have investigated the application of DNP-NMR to synthetic polymers [17], particularly insoluble polymers, which are suitable targets for solid-state NMR [18]. On the basis of our previous contributions regarding

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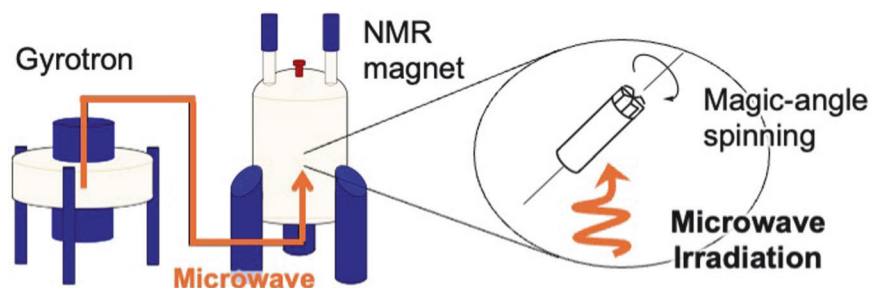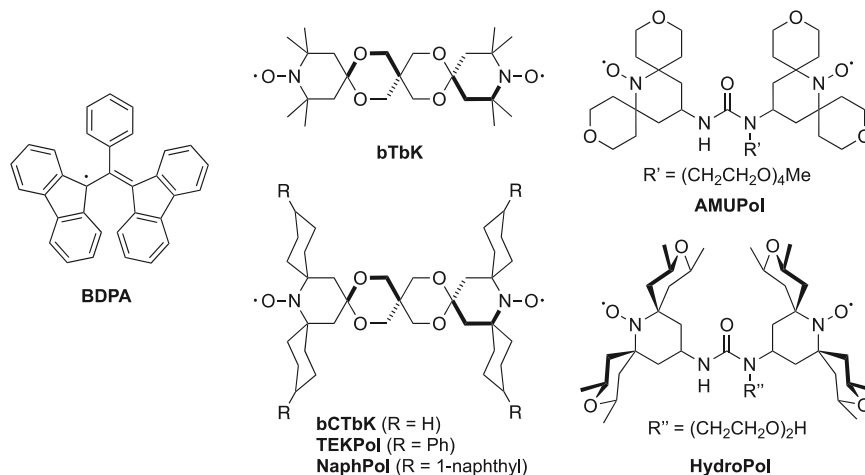Fig. 1 Schematic view of the MAS-DNP NMR system

Fig. 2 Representative radicals for the polarizing agent

PS-supported catalysts, we applied DNP-NMR to insoluble polymers. First, we developed a DNP sample preparation protocol to rationally select the optimal polarizing agent solution in accordance with the swelling properties of cross-linked PS. Furthermore, we extended our approach to high-performance engineering plastics, which are tough materials that typically have no swelling properties. A precise structural analysis of trace species in polymer-supported catalysts was also performed. In this focus review, we highlight our recent contributions to the structural analysis of polymers via DNP-NMR.

Sample preparation protocol for cross-linked polystyrene'

Cross-linked PS, which is conventionally prepared via copolymerization of styrene and divinylbenzene at an appropriate ratio, is widely used as a support for heterogeneous catalysts and ion-exchange resins. DNP-NMR measurements of linear PS were reported by Viel et al., who discussed several DNP sample preparation methods: the glass-forming method, in which the polymer is dissolved in a polarizing agent solution and frozen as is, and the film-casting method, in which a film is prepared in a solution containing the polymer and biradicals [19]. The key to these methods is the uniform dispersal of the polarizing agent throughout the polymer. For cross-linked polystyrene, however, an alternative sample preparation method should be developed because the material does not dissolve in a polarizing agent solution.

To achieve efficient DNP enhancement, we focused on the swelling properties of the polymer as a guideline for DNP sample preparation [20]. TEKPol/1,1,2,2-tetra-chloroethane (TCE) and AMUPol/dimethylsulfoxide (DMSO) solutions were selected as prototypical polarizing agents for DNP-NMR measurements, and the affinity of these solutions for the polymer is crucial for homogeneous distribution of the biradicals involved. First, we tested the swelling volume of cross-linked PS (Fig. 3a) in TCE and DMSO. Pristine PS (**1**) swelled more in TCE than in DMSO, whereas PS modified with NMe_3Cl (**3a**) exhibited the opposite swelling trend (Fig. 3b, c). The ratio of the ^{13}C signal sensitivity under microwave on/off conditions (ε_C) was studied using TEKPol/TCE and AMUPol/DMSO as polarizing agents. In this study, the ε_C values were estimated on the basis of an integral of aromatic signals (120–150 ppm). The ε_C values were greater when the PS beads were efficiently swelled (Fig. 3d–g). In fact, the plot of ε_C versus swelling volume for various cross-linked PSs (**1, 2, 3a-f**) with various alkyl chain lengths of alkylammonium salts demonstrated a correlation for both TEKPol/TCE and AMUPol/DMSO (Fig. 3h, i). For TEKPol/TCE, a linear relationship was obtained for PS modified
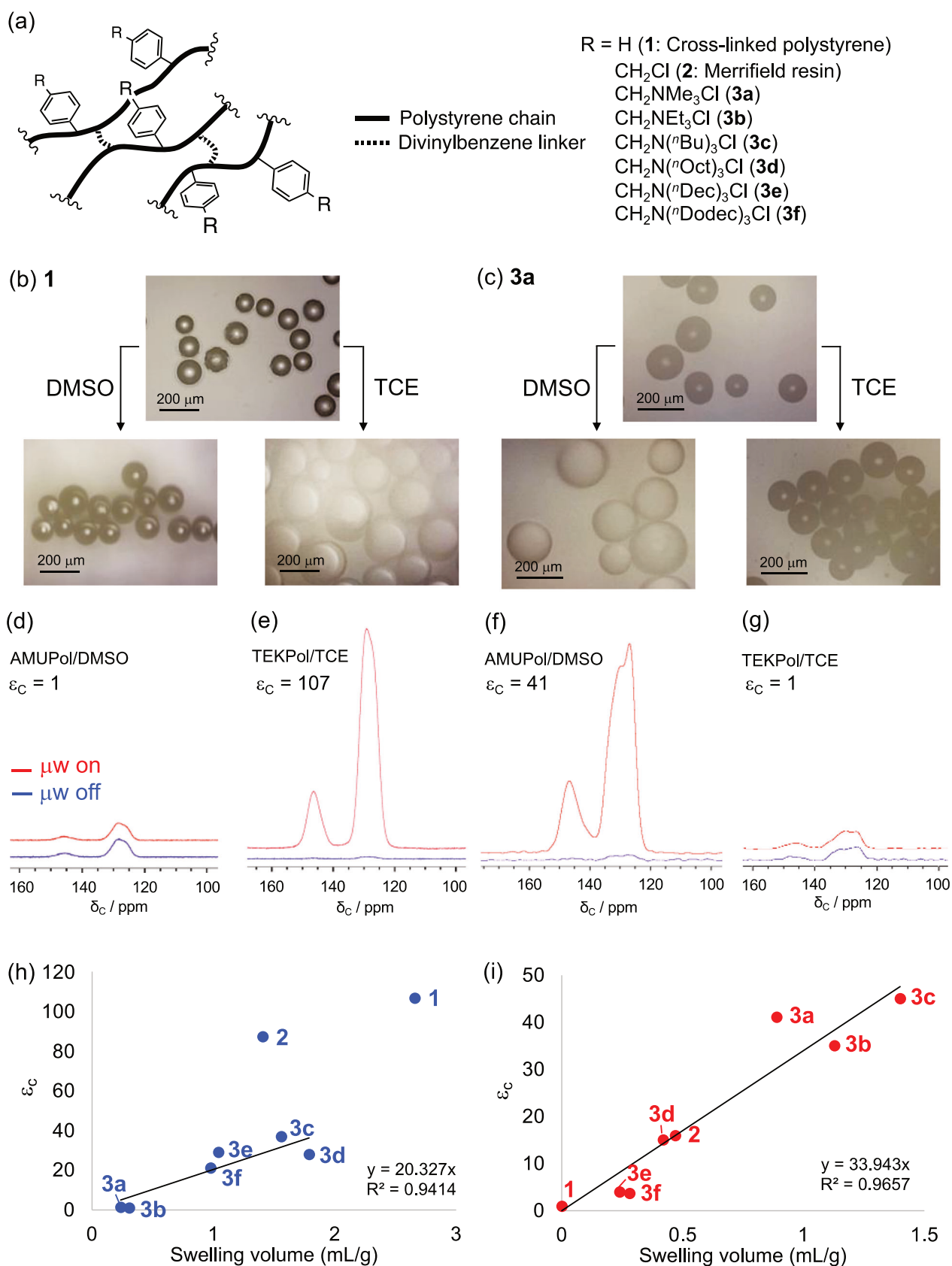
Fig. 3 Structures of pristine PS (**1**), Merrifield resin (**2**), and PS modified with quaternary alkyl ammonium salts (**3a–f**) (**a**). Photographs of polymer beads before and after swelling (**b, c**), and DNP-enhanced $^{13}C\{^{1}H\}$ CPMAS NMR spectra of **1** (**d, e**) and **3a** (**f, g**) recorded with AMUPol/DMSO and TEKPol/TCE. Plots of ε_C versus swelling volume for TCE (**h**), and that for DMSO (**i**). These values are determined by the ^{1}H–^{13}C CP experiment. Figures are reproduced from ref. [20]

Fig. 4 DNP-enhanced $^{15}N\{^1H\}$ CPMAS NMR spectra of **3a–f** recorded with AMUPol/DMSO (for **3a–d**) and TEKPol/TCE (for **3e** and **3f**)
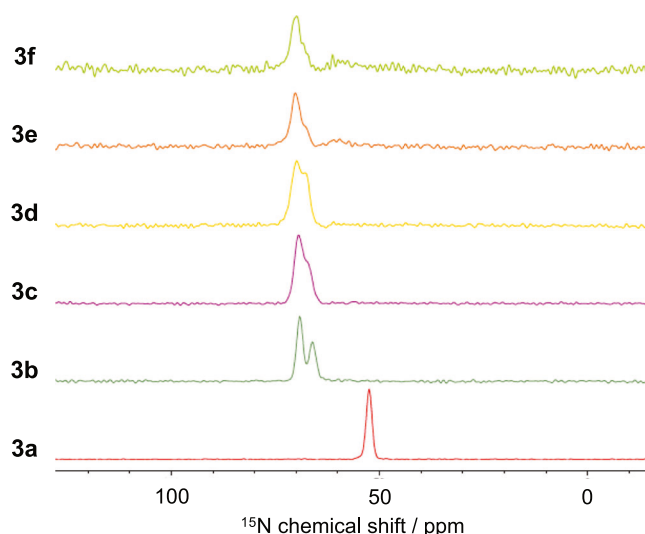
with ammonium salts (**3a-f**), whereas higher values were obtained for pristine PS (**1**) and chloromethylated PS (**2**). Compared with polymers bearing ammonium salt, outliers **1** and **2** are likely attributed to closer interfacial contact between radicals and polymer chains. A linear relationship was also obtained for AMUPol/DMSO, including for **1** and **2**. On the basis of the optimized conditions, we structurally analyzed various alkylammonium salts supported on PS by DNP ^{15}N NMR at a ^{15}N natural abundance level (0.37%). For all the polymers studied, ^{15}N signals with acceptable signal–to–noise ratios were observed within several hours of measurement, demonstrating that this method is readily accessible in synthetic studies (Fig. 4). In addition, two types of ^{15}N signals were observed for polymers (**3b-f**) with more than two alkyl group carbons. For example, in **3b**, a shoulder was observed at 66.1 ppm along with the main signal at 69.0 ppm. DNP ^{15}N NMR measurements of the model molecule $BnNEt_3Cl$ under the same conditions yielded mostly identical signals, suggesting that structural isomers of the alkylammonium salt were present on PS. Furthermore, comparison of the chemical shifts with the calculated values obtained by DFT revealed that the isomers were characterized as different conformations of the alkyl groups (conformers) around the quaternary nitrogen [21, 22].

## End-group characterization of poly(phenylene sulfide)

High-performance engineering plastics are widely used as alternatives for metallic materials because of their high mechanical strength, heat resistance, and chemical resistance [23–25]. In addition to being useful monomaterials, they are also useful as polymer composites combined with other organic as well as inorganic materials, and increased demand is expected in the near future. To develop composite materials rationally, an in-depth understanding of the structure of the polymer chain is necessary. High-performance engineering plastics, however, have intrinsic features making structural characterization by classical analytical methods almost inapplicable at the cost of high chemical stability. Thus, the development of a novel analytical method that is suitable for such engineering plastics is highly desirable. We aimed to apply DNP-NMR to the structural analysis of engineering plastics and selected polyphenylene sulfide (PPS) as a model material. As PPS does not possess swelling properties in common organic solvents, a novel sample preparation method available for PPS was investigated [26].

First, the TEKPol/TCE solution was selected as the polarizing solution for powdered PPS. The DNP sample was prepared via the incipient wetness impregnation (IWI) method. The DNP signal enhancement of the ^{13}C signal of PPS, however, was low ($\varepsilon_{C,PPS}$: ~4). Because the distribution of TEKPol in the PPS polymer network was apparently insufficient, we next examined the following heating treatment: PPS and the TEKPol/TCE solution were mixed and heated at 60 °C or 100 °C in an NMR sample rotor, and ^{13}C CPMAS measurements were obtained for the sample to determine $\varepsilon_{C,PPS}$ over time. The results showed that heating at 60 °C efficiently increased $\varepsilon_{C,PPS}$, whereas heating at 100 °C decreased $\varepsilon_{C,PPS}$ over time due to the thermal decomposition of biradicals (Fig. 5). Further optimization of the polarizing agent concentration and solvent yielded the maximum $\varepsilon_{C,PPS}$ (~40) when 1-chloronaphthalene (1-CN) was used.

The presence of the ring-opened product of N-methylpyrrolidone (NMP), which is used in the polymerization reaction as a solvent, at the PPS polymer end was

Fig. 5 Time-course study of $\varepsilon_{C,PPS}$ determined with PPS samples treated at rt, 60 °C, and 100 °C. This figure was reproduced from ref. [26] with permission from the American Chemical Society
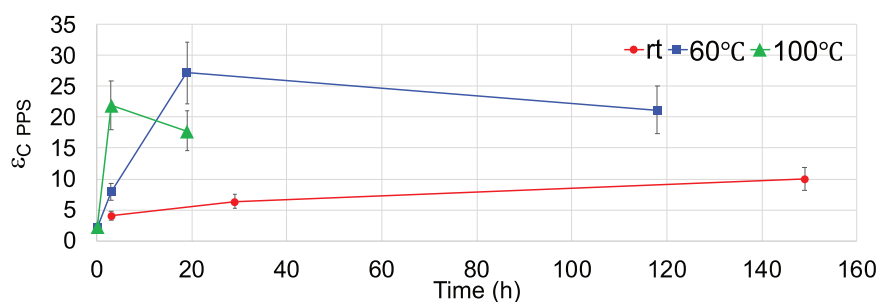
previously reported, but no definitive evidence was provided. DNP ^{13}C CPMAS measurements of samples prepared under optimized conditions revealed signals due to the end group at 24, 34, 39, 52, 156, and 183 ppm (Fig. 6). Furthermore, DNP ^{15}N CPMAS measurements revealed a signal at 62 ppm (Fig. 7). By comparing the observed chemical shifts with those observed from the measurement of synthesized model molecules (**4-7**) under the same conditions (Fig. 6), we determined the presence of a sodium carboxylate salt (model structure: **4**) at the end group of PPS. The presence of sodium salt was also evidenced by atomic absorption spectroscopy, which indicated that PPS contains 0.11 mmol/g of Na. These results provide reliable structural information for the development of PPS-based composite materials. In addition, they clearly demonstrate the involvement of the secondary amine moiety of the NMP-derived ring-opened product in the termination step of the PPS polymerization reaction.

Characterization of polymer-supported catalysts

Polymer-supported catalysts have practical advantages in that they can be easily recovered and reused and can be applied to continuous flow-type reactions by packing them into columns [27]. Whereas molecular catalysts can be precisely characterized by solution NMR and other analytical methods, analytical methods suitable for polymer-supported catalysts are limited, making rational catalyst design difficult. In this context, DNP-NMR serves as a powerful analytical method for polymer-supported catalysts.

Earlier, we developed an alkylammonium salt catalyst for the synthesis of glycidyl esters by the transesterification reaction between methyl esters and glycidol [28]. The catalyst worked well in a homogeneous manner as well as in a cross-linked PS-supported heterogeneous manner, but direct analysis of the catalyst embedded in the PS polymer network was difficult, preventing us from optimizing the structure and discussing the reaction mechanisms. We thus applied DNP ^{15}N NMR for structural analysis of the PS-supported alkylammonium salt catalyst using a ^{15}N natural abundance sample [29]. On the basis of precise characterization of the catalyst, we synthesized various PS-supported alkylammonium salt catalysts that are active for the transesterification reaction (Fig. 8a). After the structure was optimized, we found that an alkylammonium salt with two octyl groups and a methyl group was highly active in the transesterification reaction. Notably, the catalytic activity did not decrease even after reusing the catalyst more than three times. We further examined DNP-enhanced ^{1}H-^{15}N HETCOR using a nitrate anion-type catalyst mixed with glycidol. The 2D spectra clearly showed a signal due to the ring-opened product derived from glycidol and nitrate, indicating that the alkoxide species behaves as an active catalyst (Fig. 8b). Moreover, we extended this approach to another polymer-supported catalysts: a polyethyleneimine (PEI)-supported Ir catalysts [30]. This catalyst is highly active in the decomposition of formic acid, which is a useful method for recovering hydrogen from a portable liquid hydrogen carrier. Notably, the catalyst is available in the form of a column reactor, in which hydrogen gas is generated continuously simply by flowing formic acid. In this contribution, DNP-NMR offered a precise characterization of the catalyst species. On the basis of DNP ^{15}N NMR and ^{13}C NMR, we confirmed that the Ir complex possesses a pentamethylcyclopentadienyl (Cp*) group and a bipyridine ligand immobilized on a PEI network. Because such a ligand structure around the Ir center is critical for high activity, we concluded that the catalyst works in a heterogeneous manner.

Summary

This focus review highlights our recent contributions to solid-state DNP-NMR measurement techniques for insoluble polymeric materials. We first described the DNP sample preparation protocol for cross-linked PS, which is commonly used in the fields of catalysis and organic synthesis. We also established an effective DNP sample preparation method for high-performance engineering plastics and characterized the PPS end groups. Moreover,

Fig. 6 DNP-enhanced ^{13}C CPMAS NMR spectra of model compounds **4, 5, 6, 7** and PPS. The signal with an asterisk corresponds to an impurity in the polarizing solution. SSB represents the spinning sideband of PPS and 1-CN. All the spectra were recorded at 110–112 K. This figure was reproduced from ref. [26] with permission from the American Chemical Society
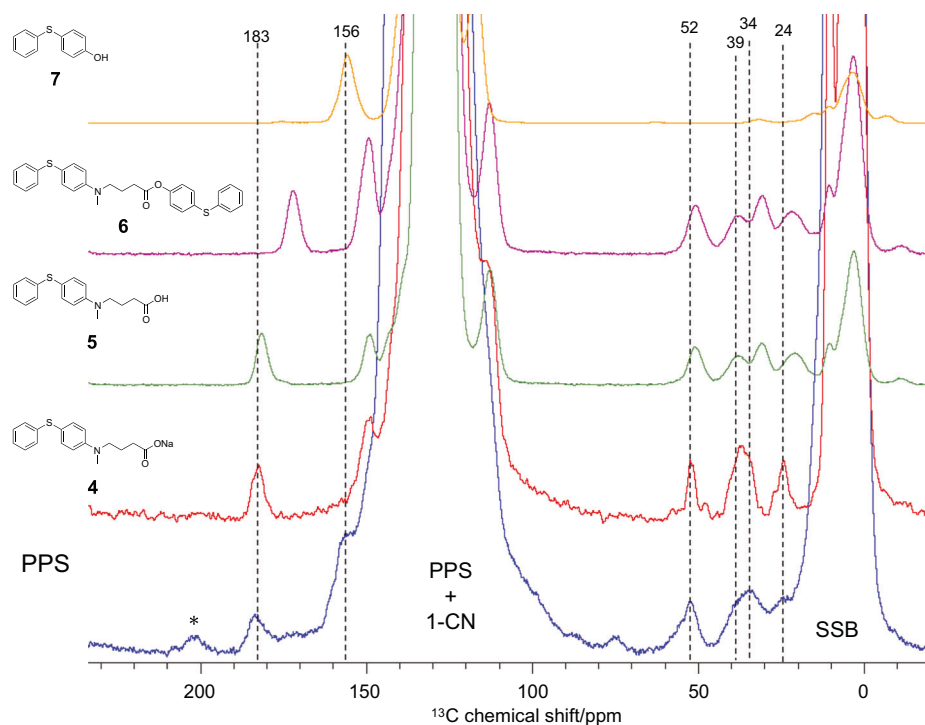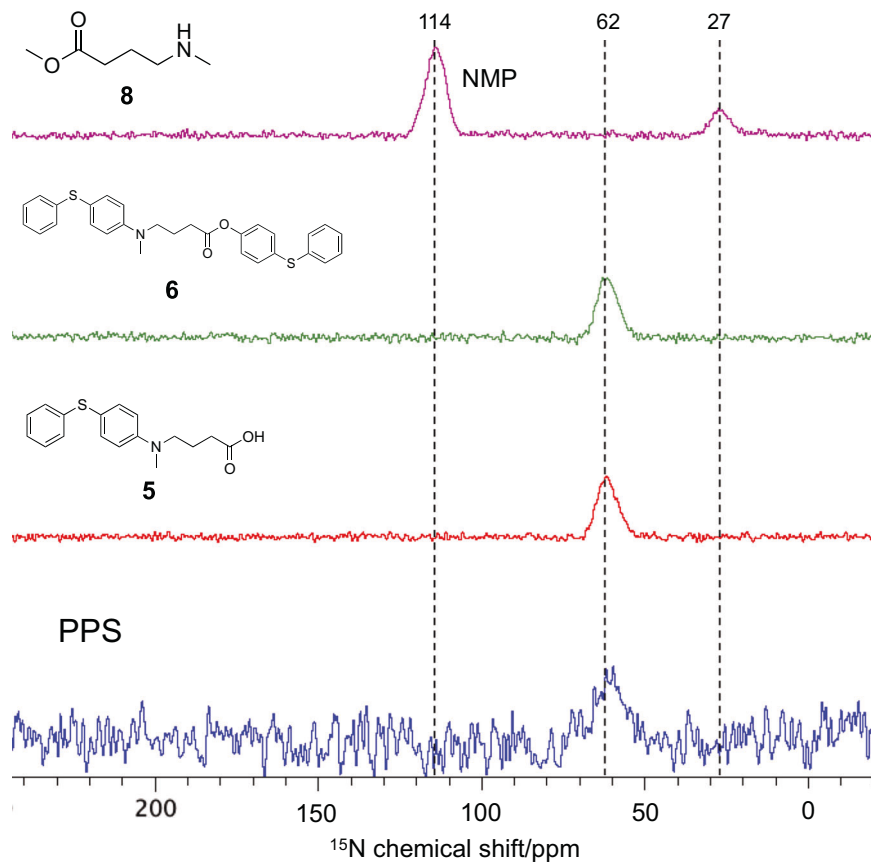

Fig. 7 DNP-enhanced ^{15}N CPMAS NMR spectra of model compounds **5, 6, 8**, and PPS. All the spectra were recorded at 110–112 K. This figure was reproduced from ref. [26] with permission from the American Chemical Society
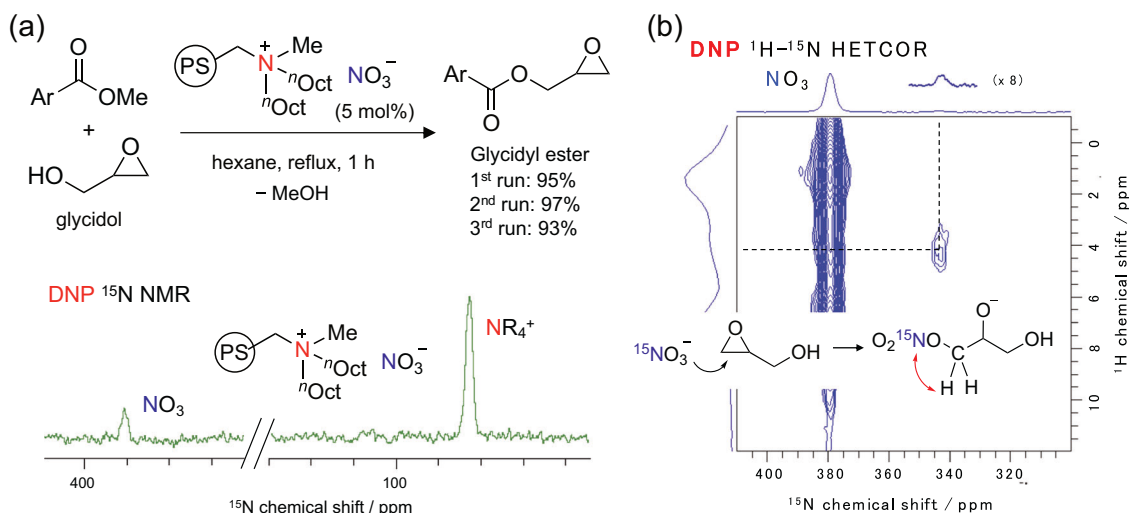
Fig. 8 Synthesis of glycidyl ester by catalytic transesterification of methylester with glycidol. PS-supported quaternary alkylammonium salts were structurally characterized via DNP-enhanced ^{15}N NMR and utilized as catalysts (**a**). The ring-opened product generated by the catalyst with glycidol was observed by DNP ^{1}H-^{13}C HETCOR (**b**)

we expanded the scope of application to various polymer-supported catalysts. Further application toward hybrid polymer materials, polymer-supported catalysts, biodegradable polymers, and surface analysis of chemically treated polymers is ongoing in our group.

Compliance with ethical standards

Conflict of interest The author declares no competing interests.

References

1. Kuptsov AH, Zhizhin GN. Handbook of fourier transform raman and infrared spectra of polymers, Elsevier, 1998.
2. Wesdemiotis C, Williams-Pavlantos KN, Keating AR, McGee AS, Bochenek C. Mass spectrometry of polymers: a tutorial review. Mass Spectrom Rev. 2023;43:427–76.
3. Chu B, Hsiao BS. Small-angle X-ray scattering of polymers. Chem Rev 2001;101:1727–62.
4. Wei Y, Hore MJA. Characterizing polymer structure with small-angle neutron scattering: a tutorial. J Appl Phys 2021;129:171101.
5. Hatada K, Kitayama T, NMR spectroscopy of polymers, Springer, 2004.
6. Hansen MR, Graf R, Spiess HW. Interplay of structure and dynamics in functional macromolecular and supramolecular systems as revealed by magnetic resonance spectroscopy. Chem Rev 2015;116:1272–308.
7. Michaelis VK, Griffin RG, Corzilius B, Vega S, ed. Handbook of high-field dynamic nuclear polarization, John Wiley & Sons, 2020.
8. Overhauser AW. Polarization of nuclei in metals. Phys Rev. 1953;92:411–5.
9. Afeworki M, McKay RA, Schaefer J. Selective observation of the interface of heterogeneous polycarbonate/polystyrene blends by dynamic nuclear polarization carbon-13 NMR spectroscopy. Macromolecules. 1992;25:4084–91.
10. Afeworki M, McKay RA, Schaefer J. Dynamic nuclear polarization enhanced nuclear magnetic resonance of polymer-blend interfaces. Mater Sci Eng: A. 1993;162:221–8.
11. Becerra LR, Gerfen GJ, Temkin RJ, Singel DJ, Griffin RG. Dynamic nuclear-polarization with a cyclotron-resonance maser at 5-T. Phys Rev Lett. 1993;71:3561–4.
12. Horii F, Idehara T, Fujii Y, Ogawa I, Horii A, Entzminger G, et al. Development of DNP-enhanced high-resolution solid-state NMR system for the char- acterisation of the surface structure of polymer materials. J Infrared Millim Terahertz Waves. 2012;33:756–65.
13. Hu KN, Yu HH, Swager TM, Griffin RG. Dynamic nuclear polarization with biradicals. J Am Chem Soc. 2004;126:10844–5.
14. Venkatesh A, Casano G, Wei R, Rao Y, Lingua H, Karoui H, et al. Rational design of dinitroxide polarizing agents for dynamic nuclear polarization to enhance overall NMR sensitivity. Angew Chem Int Ed 2024;63:e202317337.
15. Venkatesh A, Casano G, Rao Y, De Biasi F, Perras FA, Kubicki DJ, et al. Deuterated TEKPol biradicals and the spin-diffusion barrier in MAS DNP. Angew Chem Int Ed 2023;62:e202304844.
16. Kobayashi T, Perras FA, Slowing II, Sadow AD, Pruski M. Dynamic nuclear polarization solid-state NMR in heterogeneous catalysis research. ACS Catal. 2015;5:7055–62.
17. Mollica G, Ziarelli F, Thureau P, Viel S. Structural investigations of polymer materials by dynamic nuclear polarisation solid-state NMR. In NMR methods for characterization of synthetic and natural polymers 2019; 533-54.
18. Tanaka S. Ann Rep. NMR Spectrosc. 2022;105:1.
19. Le D, Casano G, Phan TNT, Ziarelli F, Ouari O, Aussenac F, et al. Optimizing sample preparation methods for dynamic nuclear polarization solid-state NMR of synthetic polymers. Macromolecules. 2014;47:3909–16.
20. Tanaka S, Liao W-C, Ogawa A, Sato K, Copéret C. DNP NMR spectroscopy of cross-linked organic polymers: rational guidelines towards optimal sample preparation. Phys Chem Chem Phys 2020;22:3184–90.
21. Naudin C, Bonhomme F, Bruneel JL, Ducasse L, Grondin J, Lassegues JC, et al. Rotational isomerism of the tetra-ethylammonium cation in solution and in the solid state. J Raman Spectrosc. 2000;31:979–85.

22. Takekiyo T, Yoshimura Y. Drastic change in the conformational equilibria of tetraethylammonium bromide in the glassy aqueous solution. Chem Phys Lett. 2006;420:8–11.

23. Melton GH, Peters EN, Arisman RK, in Applied Plastics Engineering Handbook, 2011, 7-21.

24. Oyama HT, Matsushita M, Furuta M. High performance reactive blends composed of poly(p-phenylene sulfide) and ethylene copolymers. Polym J. 2011;43:991–9.

25. Nara S, Oyama HT. Effects of partial miscibility on the structure and properties of novel high performance blends composed of poly(p-phenylene sulfide) and poly(phenylsulfone). Polym J. 2014;46:568–75.

26. Tanaka S, Takada S, Suzuki T, Nakajima Y, Sato K. End-Groups of Poly(p-phenylene sulfide) Characterized by DNP NMR Spectroscopy. Macromolecules 2022;55:2806–12.

27. Hodge P. Organic synthesis using polymer-supported reagents, catalysts and scavengers in simple laboratory flow systems. Curr Opin Chem Biol. 2003;7:362–73.

28. Tanaka S, Nakashima T, Maeda T, Ratanasak M, Hasegawa J, Kon Y, et al. Quaternary alkyl ammonium salt-catalyzed transformation of glycidol to glycidyl esters by transesterifcation of methyl esters. ACS Catal. 2018;8:1097–103.

29. Tanaka S, Nakajima Y, Ogawa A, Kuragano T, Kon Y, Tamura M, et al. DNP NMR spectroscopy enabled direct characterization of polystyrene-supported catalyst species for synthesis of glycidyl esters by transesterification. Chem Sci. 2022;13:4490–7.

30. Sawahara K, Tanaka S, Kodaira T, Kanega R, Kwanam H. Iridium catalyst immobilized on crosslinked polyethyleneimine for continuous hydrogen production using formic acid. ChemSusChem. 2024;17:åe2023012.

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