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Thermosetting polymer for dynamic nuclear polarization: Solidification of an epoxy resin mixture including TEMPO

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ABSTRACT

We investigated the dynamic nuclear polarization (DNP) of typical thermosetting polymers (two-component type epoxy resins; Araldite[®] Standard or Araldite[®] Rapid) doped with a (2,2,6,6-tetramethylpiperidine-1-yl)oxy (TEMPO) radical. The doping process was developed by carefully considering the decomposition of TEMPO during the solidification of the epoxy resin. The TEMPO electron spin in each two-component paste decayed slowly, which was favorable for our study. Furthermore, despite the dissolved TEMPO, the mixture of the two-component paste successfully solidified. With the resulting TEMPO-doped epoxy-resin samples, DNP experiments at 1.2 K and 3.35 T indicated a magnitude of a proton-spin polarization up to 39%. This polarization is similar to that (35%) obtained for TEMPO-doped polystyrene (PS), which is often used as a standard sample for DNP. To combine this solidification of TEMPO-including mixture with a resin-casting technique enables a creation of polymeric target materials with a precise and complex structure.

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1. Introduction

Dynamic nuclear polarization (DNP) is promising for a wide range of applications, including as a polarized target in nuclear and particle physics [1], highly sensitive nuclear magnetic resonance (NMR) spectroscopy [2], metabolic imaging combined with magnetic resonance imaging [3], broadband neutron spin filter [4], and contrast variation in small-angle neutron scattering (SANS) [5].

In DNP, the large electron-spin polarization in a high magnetic field and at low temperature is transferred to proton spins via microwave irradiation at a frequency near the Larmor frequency of electron spin [6]. To incorporate electron spins in a sample, beam-irradiation [7–9] and chemical-doping [10–18] techniques were developed for this purpose. In chemical doping, stable radical (2,2,6,6-tetramethylpiperidine-1-yl)oxy (TEMPO; see Fig. 1a) is known to work effectively as a source of electron spin [10]. Thus far, many groups have used a frozen-solution system in which paramagnetic species are dissolved [10].

Polymeric target systems doped with stable radicals are much easier to handle than solution systems because polymers form self-standing solids even at room temperature. In addition, polymer samples can be fabricated in the form of thin films, which can reduce internal heating by microwave irradiation for DNP.

Furthermore, very thin ($\sim\mu\text{m}$) polarized polymeric targets are now essential for experiments involving a low-transmission beam [11–14]. Free radicals can be doped into a polymeric system by solvent-casting [10,14,17] or vapor-sorption [10–13,15–18]. For the solvent-cast method, polymer and TEMPO are dissolved together, and the solution is poured into a flat-bottom dish. Evaporation of the solvent leaves a TEMPO-doped cast film in the dish. For the vapor-sorption method, polymer and TEMPO are put together in a sealed container. The TEMPO vapor spontaneously permeates the rubbery phase of the polymer; therefore, the polymer should inherit a continuous rubbery phase.

As a new class of polymeric target materials, we have focused on a thermosetting polymer, which solidifies by forming a cross-linked network via irreversible chemical reactions triggered by high temperature and/or mixing of several components [19]. This solidification process is called “curing”. A merit of thermosetting polymers is that a resin-casting technique can be used. For resin casting, the resin shrinkage after solidification is very small because no volatile solvent is involved. Therefore, we can fabricate precise complex structures such as self-standing curved plates, and lenses with concave or convex surface.

Because neutron scattering phenomena are highly sensitive to proton spin polarization (P_H), proton spin polarization has a significant potential in neutron optical devices. In this direction, Eichhorn et al. recently developed a broadband neutron spin filter for practical use, which is composed of an organic crystal at photo-excited triplet DNP states [4]. As other possibilities, if we make a lensed polymeric target, it can work as a neutron lens with

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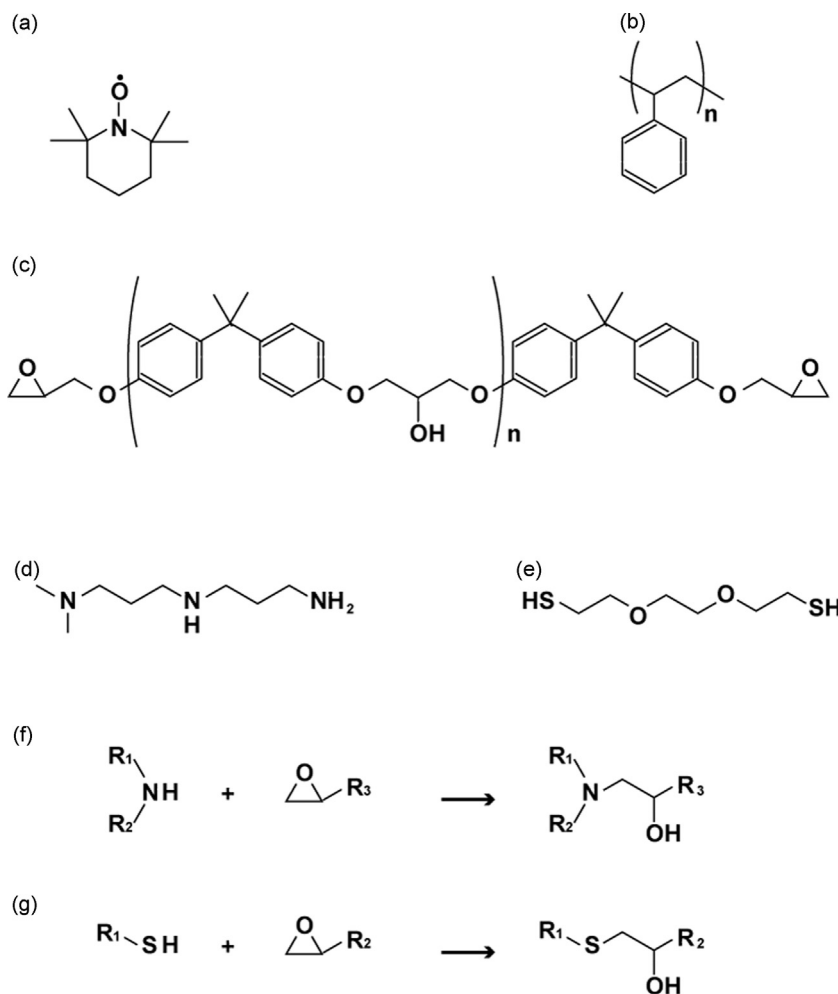


Fig. 1. Chemical structure for (a) TEMPO free radical, (b) polystyrene (PS), and the reagents included in the epoxy-resin pastes: (c) diglycidyl ether of bisphenol A (DGEBA), (d) *N,N*-dimethyldipropylenetriamine (DMAPAPA), and (e) 2,2'-(ethylenedioxy)diethanethiol. Reaction schemes for crosslink formation between (f) amine and epoxy and (g) thiol and epoxy.

adjustable focal length. The adjustable focal length arises because the index of refraction n for neutrons is given by $n = 1 - (\lambda^2/\pi) \sum b_i N_i$, where λ is the neutron wavelength, and b_i and N_i are the scattering length and number density of elements within the target material [20,21], respectively. The scattering length b_H of protons against a fully polarized neutron depends strongly on P_H : $b_H = (-0.374 + 1.456P_H) \times 10^{-12}$ cm [22].

Furthermore, epoxy resins can bind well on metal or ceramic surface. This property is favorable for the use at very low temperature. In addition, the physical properties of epoxy resins can be tailored by introducing filler particles (silica, clay, etc.) [19]. As a commercial cryogenic epoxy (SK-229, Nitto Denko), a filler introduction can improve a heat-shock resistance, which is favorable for the use under cryogenic conditions.

Researches of materials science have been increasingly attracted by a structure formed by fillers in thermosetting resin composites [23,24]. The nanometer-scale structure of these materials can be determined by SANS with contrast variation [5,15–18]. A composite system including epoxy resins is a promising candidate for future spin-contrast-variation SANS studies.

With these motivations in mind, we developed a TEMPO-doping technique for epoxy resin and investigated the DNP of the resulting TEMPO-doped epoxy resin. As a control, we also studied TEMPO-doped polystyrene (PS; see Fig. 1b). In DNP experiments, PS is often used as a matrix for incorporating free radicals [10,14].

2. Experiment

2.1. Sample preparation

2.1.1. TEMPO-doped epoxy resin

For a source of electron spin for DNP, we used the TEMPO radical from TCI without further purification. As two-component epoxy adhesives, we used Araldite[®] Standard (referred to as “AS”) and Araldite[®] Rapid (referred to as “ARAR”) by Huntsman Advanced Materials, because of their wide availability. Each of them is composed of a resin and hardener pastes. After mixing the two pastes, it takes 12 h for AS and 1 h for AR to solidify at ambient temperature.

According to the material safety data sheets (MSDSs) by Huntsman Advanced Materials [25], the resin pastes of AS and AR contain 60–100% diglycidyl ether of bisphenol A (DGEBA), which contains epoxy groups at both ends, as shown in Fig. 1c. Since DGEBA we used has a molecular weight (MW) of less than 700, the number “ n ” in Fig. 1c is 0 or 1. The AS hardener paste contains 7–13% *N,N*-dimethyldipropylenetriamine (DMAPAPA; see Fig. 1d) and other polyamine compounds (not shown). The AR hardener paste contains 1–3% DMAPAPA, 1–3% 2,2'-(ethylenedioxy)diethanethiol (Fig. 1e), and several tertiary amine compounds (not shown). The combination of polythiol and a tertiary amine is frequently used for fast-cure adhesives, because the tertiary amine catalyzes the reaction of polythiol with epoxy [19].

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