Mechanochemistry

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Mechanophores with a Reversible Radical System and Freezing-Induced Mechanochemistry in Polymer Solutions and Gels**

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Abstract: *Visualization and quantitative evaluation of covalent bond scission in polymeric materials are highly important for understanding failure, fatigue, and deterioration mechanisms and improving the lifetime, durability, toughness, and reliability of the materials. The diarylbibenzofuranone-based mechanophore radical system enabled, through electron paramagnetic resonance spectroscopy, in situ quantitative evaluation of scission of the mechanophores and estimation of mechanical energy induced along polymer chains by external forces. The coagulation of polymer solutions by freezing probably generated force but did not cleave the mechanophores. On the other hand, cross-linking led to efficient propagation of the force of more than 80 kJ mol^{-1} to some mechanophores, resulting their cleavage and generation of colored stable radicals. This mechanoprobe concept has the potential to elucidate other debated issues in the polymer field as well.*

Macroscopic mechanical forces applied to polymeric materials, such as tension, compression, and shear loading, are known to be transferred to each polymer chain, resulting in chemical reactions and scission of covalent bonds and non-covalent interactions.[1–13] Force is also generated along polymer chains by sonicating polymer solutions[4,10,14–21] and swelling cross-linked polymers.[22] Heating commonly induces force or distortion in polymer chains because the molecular motion of the chains is activated with temperature. Conversely, cooling seems to stabilize bonds in polymers because of the decreased motion of the polymer chains. However, some researchers have reported that freezing polymer solutions can induce polymer chain scission.[23–27] This phenomenon was considered to result from polymer chain adhesion to solvent crystallites that formed upon freezing. The observation of decreased solution viscosity and the increased retention volume of size-exclusion chromatography (SEC) were regarded to result from degradation of the polymer chains. On the other hand, Qian and co-workers suggested that freezing polymer solutions did not generate polymer chain degradation, but instead altered the single-chain polymer morphology to a more compact coil owing to the formation of intra-chain cohesion entanglements.[28] AFM observations of single-chain polystyrene particles revealed that the morphology changed to a smaller coil size when the polymer solution was frozen, but recovered to that observed before freezing by heating to 100 °C. The work of Cheng and co-workers supported this observation because the molar mass of polystyrene calculated from SEC decreased by freezing the solution but recovered by heating to 100 °C.[29,30] Some reports have also indicated that freezing a poly(ethylene oxide) solution induces a unique polymer chain conformation, which is only found under elongation force field.[31,32] These studies suggest that freezing polymer solutions does not generate polymer chain scission but conformational changes. Therefore, whether freezing polymer solutions actually induces mechanical force along the polymer chains and if so, the magnitude of the force generated, remains unclear.

In this study, we resolved these questions by using a new mechanically sensitive probe (mechanophore), diarylbibenzofuranone (DABBF; Figure 1 a). DABBF and its corresponding radicals are in equilibrium at room temperature without the formation of by-products (reversible), though the amount of radicals formed is quite small.[33–36] The radicals are blue-colored and show greatly reduced reactivity toward oxygen.[37–39] Because of these distinctive properties, this radical system enables in situ quantitative evaluation of polymer chain scission through electron paramagnetic spectroscopic (EPR) studies, unlike previously reported mechanophores.[1–22] We investigated the response of DABBF linkages incorporated in a linear polymer and a polymer network to the freezing of solutions and gels, and calculated the bond dissociation energies (BDEs) for the central C–C bonds in the linkages as an indicator to estimate the magnitude of the force generated along the polymer chains.

Before introducing DABBF into polymer structures, the equilibrium, BDEs, and mechanoresponsiveness of DABBF monomers (Figure 1 b) were inspected using EPR measurements. Figure 2 a shows the EPR spectra of a 100 mM solution

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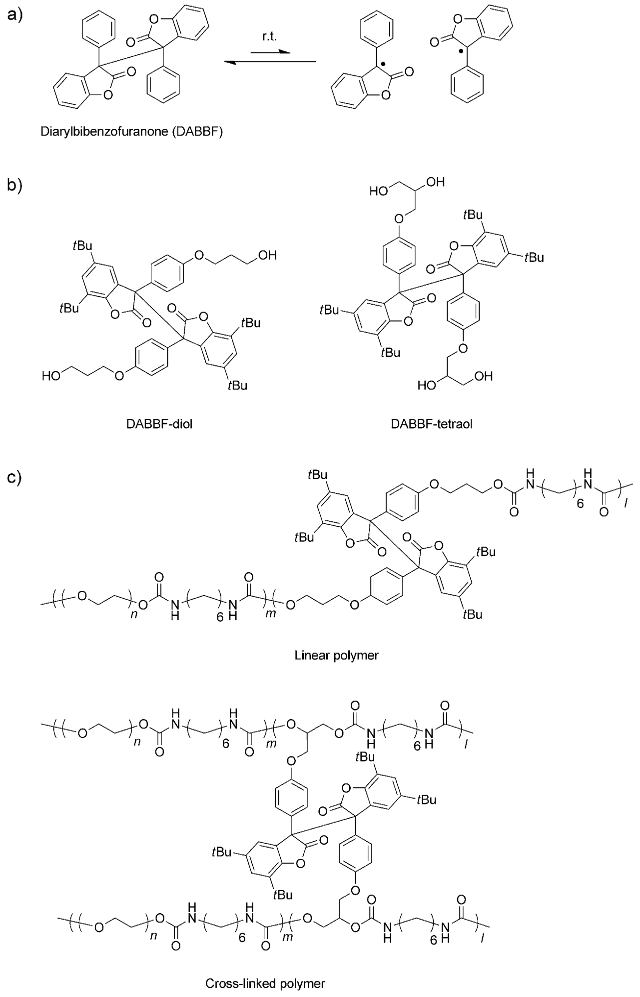

Figure 1. a) Equilibrium between DABBF and its corresponding radicals. b) DABBF monomers used to produce polymers. c) Linear polymer and cross-linked polymer with DABBF linkages.

of the dihydric DABBF monomer (DABBF-diol) in benzene measured in the temperature range from −100 to 50 °C. The *g* value of these spectra was determined to be 2.0037, suggesting the presence of oxygen radicals and carbon radicals. Therefore, the detected spectra were attributed to the radicals formed from the cleavage of DABBF-diol (Supporting Information, Figure S1). The intensity of the peaks were negligible below 0 °C, but increased with temperature, whereas the spectral shape showed little change with temperature. These results indicate that the equilibrium of DABBF-diol shifted to the dissociated side as the temperature increased. We assumed that this equilibrium involves DABBF-diol and the dissociated radicals, without irreversible side reactions; under this assumption, we calculated the ratio of the dissociated DABBF-diol from the peak intensity by using 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL) as a standard (Figure 2 b). The ratio was extremely low below 0 °C ($< 0.0003\,\%$), indicating that almost all DABBF-diol existed as the bonded monomer. Above 0 °C, the amount of the radicals increased exponentially with increasing temperature. DABBF-diol and the tetrahydric DABBF monomer (DABBF-tetraol) both showed similar behavior in other solvents at several concentrations (Supporting Information, Figure S2–S7).

The BDEs (ΔH) and dissociation entropies (ΔS) for the central C−C bonds in the monomers were estimated from van't Hoff plots; ΔH and ΔS can be determined from the slope and intercept of the plots, respectively. Figure 2 c shows the van't Hoff plot for DABBF-diol in benzene (100 mM). The plots for the monomers in several solvents at several concentrations were also obtained (Supporting Information, Figure S8 and S9). The ΔH values for both monomers are similar and show a clear dependence on the solvent (Supporting Information, Tables S1 and S2). The obtained ΔH values of 85.4–104.8 kJ mol^{-1} are quite unique as the values are smaller than typical C−C bonds (ethane, ca. 380 kJ mol^{-1})[40] but larger than supramolecular interactions (hydrogen bonding, 8–30 kJ mol^{-1}).[41] Therefore, the central C−C bonds in the monomers are likely to dissociate preferentially to other covalent bonds in response to mechanical forces. The determined ΔH values are in agreement with those estimated from UV/Vis absorption measurements for other DABBF derivatives in toluene (95.4–98.7 kJ mol^{-1}), and the ΔS values (93.0–158.4 J K^{-1} mol^{-1}) are also reasonable for a dissociation of this type of bond.[33]

To investigate whether the monomers can act as mechanophores, we applied shear force to the powder of the monomers at 25 °C in air. The colorless powder of DABBF-diol turned blue when ground in a mortar (Figure 2 d). The blue color gradually faded over days or weeks, whereas the color immediately vanished by adding a good solvent because of the increased molecular mobility. This behavior was repeatedly observed. EPR studies on the powder before and after grinding revealed that the blue-colored powder exhibited a strong signal (Figure 2 e). The spectrum after grinding was considered to originate from the radicals formed from cleaved DABBF-diol because the *g* value and spectral shape were similar to those before grinding. The quantitative evaluation of the EPR spectra showed that a significant amount of DABBF-diol was dissociated after grinding for 30 min (from 0.0002 % to 0.0741 %). DABBF-tetraol also showed similar behavior (Supporting Information, Figure S10). These results indicate that the monomers experienced homolytic bond cleavage and formed colored radicals in response to shear force, and therefore can work as mechanophores.

A linear polymer and a cross-linked polymer with DABBF linkages (Figure 1 c) were synthesized by polyaddition of DABBF-diol or DABBF-tetraol, respectively, poly(ethylene glycol) (PEG) ($M_n = 1000$), and hexamethylene diisocyanate (HDI) in the presence of the catalyst di-*n*-butyltin dilaurate. Solutions of the linear polymer in 1,4-dioxane at several concentrations were prepared and frozen to liquid nitrogen temperature, but no color change was observed. EPR studies of these solutions during the cooling process from 50 to −100 °C revealed that the intensity of the peaks and the ratio of the dissociated linkages were only observed to decrease during the process (Figure 3 a; Supporting Information, Figure S11). The ΔH value for the linkages in the linear polymer in 1,4-dioxane was determined to be 85.1 kJ mol^{-1} (Supporting Information, Figure S12 and Table S3). Therefore, we concluded that mechanical energy

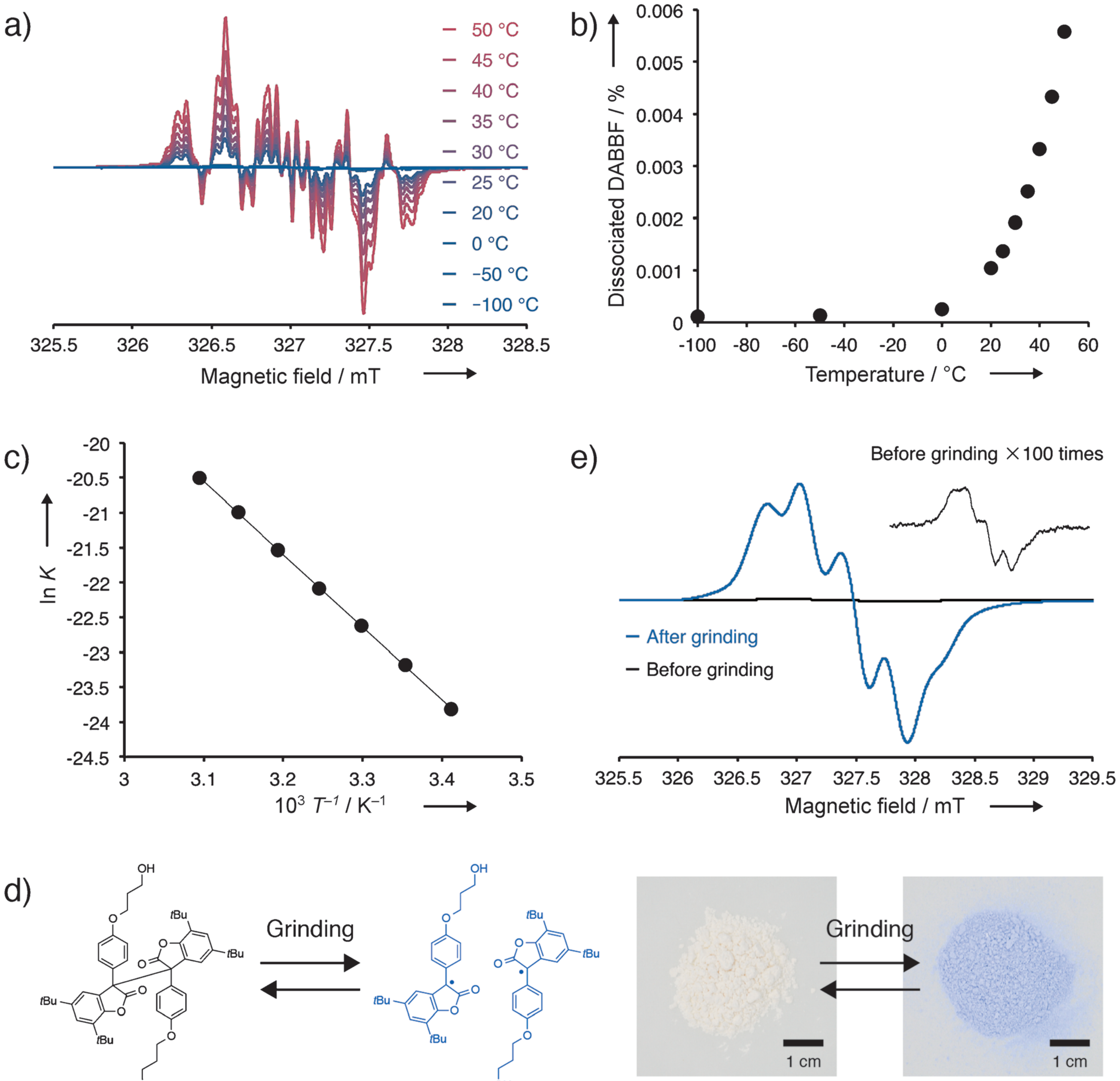

Figure 2. a) EPR spectra of a 100 mм solution of DABBF-diol in benzene in the temperature range from −100 to 50 °C. b) Percentage of dissociated DABBF-diol in benzene (100 mм) in the temperature range from −100 to 50 °C. c) van't Hoff plot for the disassociation of DABBF-diol in benzene (100 mм). d) Chemical structures, photographs, and e) EPR spectra of the powder of DABBF-diol before and after grinding at 25 °C in air.

of more than 85.1 kJ mol^{-1} was not generated along each polymer chain during freezing of the solutions.

On the other hand, the cross-linked polymer when swollen with 1,4-dioxane forms a gel that turned brilliant blue when frozen to liquid nitrogen temperature in air (Figure 3 b; Supporting Information, Movie S1). The blue color completely vanished when the gel was warmed to room temperature, and this behavior was observed repeatedly (Supporting Information, Figure S13). To confirm that the blue color originated from the dissociation of the DABBF linkages, the EPR spectra of the gel were measured during the cooling process from 50 to −100 °C (Figure 3 c). The *g* value of these spectra was determined to be consistent with oxygen radicals and carbon radicals (2.0038), indicating that the signal could be assigned to the cleaved DABBF radicals. The intensity of the peaks initially decreased with decreasing temperature because the equilibrium shifted to the bonded linkages, but a sudden increase in the intensity was observed at 4 °C. Following this increase, the spectra broadened, probably because of coagulation of the solution and a subsequent decrease in the mobility of the radicals. Figure 3 d shows the ratio of the dissociated linkages in the gel during the cooling process. While the ratio initially decreased with decreasing temperature, a steep increase was observed at 4 °C and up to 258 times more radicals were generated during freezing. The radical generation by coagulation of the 1,4-dioxane solution

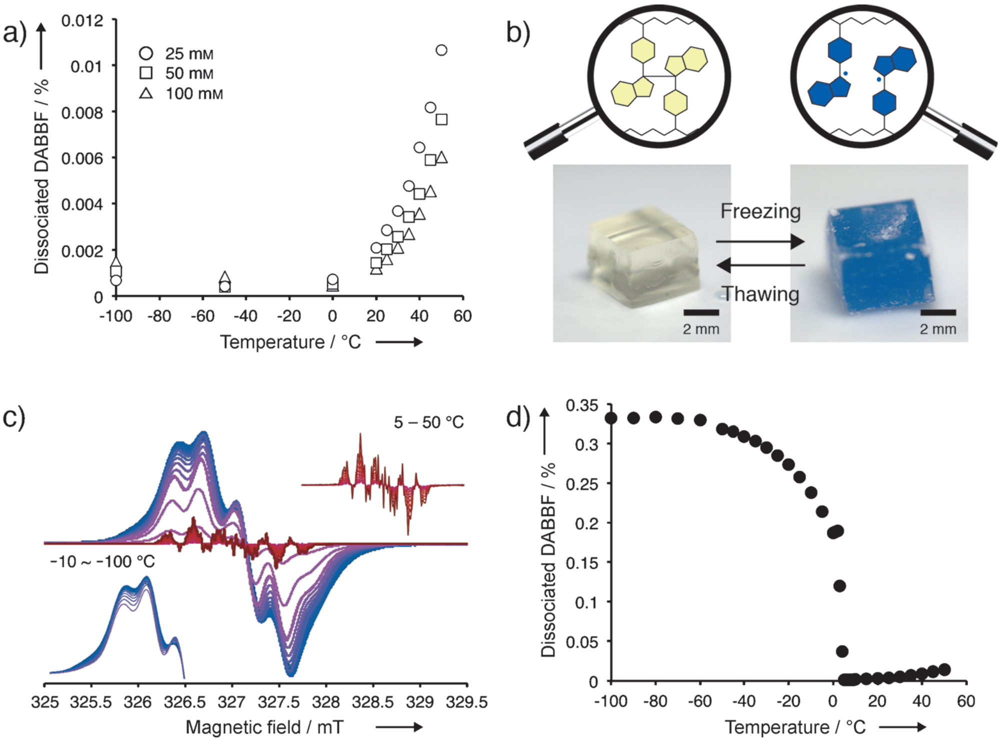

Figure 3. a) Percentage of dissociated DABBF linkages in the linear polymer in 1,4-dioxane at 25 mM (○), 50 mM (□), and 100 mM (△) during the cooling process from 50 to −100 °C. b) Photographs of the gel swollen with 1,4-dioxane before and after freezing to liquid nitrogen temperature in air. c) EPR spectra of the gel during the cooling process from 50 to −100 °C. d) Percentage of dissociated DABBF linkages in the gel during the cooling process.

was also supported by UV/Vis absorption measurements (Supporting Information, Figure S14). The freezing point depression of 1,4-dioxane in the gel (the freezing point of 1,4-dioxane is 11.8 °C) was probably due to supercooling and an inhibition of nucleation by the polymer network. We also performed a control experiment in which the DABBF moiety was not covalently attached to a similar network, but dissolved in the swelling solvent (Supporting Information, Figure S15). The control gel did not show blue color change by freezing. Additionally, the linkages in the dry cross-linked polymer were not dissociated by freezing (Supporting Information, Figure S16). These results indicate that freezing the gel and the subsequent solvent crystallization generated mechanical force along the polymer chains, resulting in the dissociation of the linkages. Therefore, we found that cross-linking is a key factor to efficiently propagate the freezing-induced force through the polymer chains. Because the ΔH value for the linkages in the gel was determined to be 81.0 kJ mol^{-1} (Supporting Information, Figure S12 and Table S3), mechanical energy of more than 81.0 kJ mol^{-1} would be generated along some polymer chains during freezing of the gel.

Color changes were not observed with the cross-linked polymer in the dry and gel states in response to any other mechanical forces, such as tension, compression, shear loading, cracking, and swelling. This is probably because the structure was not designed to efficiently transmit such macroscopic forces to the linkages and because the dissociated radicals re-combined too quickly for a color change to be observed due to the high chain motion even if the linkages were cleaved in response to the forces. On the other hand, coagulation of the solution significantly decreased the chain motion, which prevented the re-combination, and therefore we could observe the color change of the gel. Additionally, we found that activation of DABBF linkages incorporated in polymers by tension, compression, and shear loading seems to be possible by proper design of the polymer structure (work in progress). The ratio of the dissociated linkages after freezing was relatively small (< 0.5 %) because the crystal dimensions of the solvent are several orders of magnitude larger than the size of the polymer chains.[27]

The ΔH values for the linkages in the linear polymer solution and the gel were smaller than those for the monomers in 1,4-dioxane, and the values tended to decrease with the increasing number of polymer chains connected to the linkages. The ΔS values also showed a similar trend (Supporting Information, Table S3). These results may indicate that the thermal mobility and large entropy of the polymer chains caused the cleavage of the linkages to be enthalpically easier and entropically more difficult. Therefore, the equilibrium states of the mechanophores incorporated in the polymers were distinctly different from those of the monomers. Such evaluation is difficult for other mechanophores because of the lack of the ability to quantitatively estimate activated species.

We investigated the effect of solvent on the freezing-induced force. The gels swollen with some solvents did not show the blue color when frozen (Supporting Information, Table S4). We performed EPR studies during the cooling process from 50 to −150 °C on the uncolorable gels swollen with anisole and tetrahydrofuran (THF). In contrast with the behavior of the 1,4-dioxane gel, the intensity of the peaks and the ratio of the dissociated linkages in the anisole and THF gels only decreased during the cooling process (Supporting Information, Figures S17–S19). The ΔH and ΔS values for the linkages in the uncolorable gels were also evaluated, but were not found to correlate with the force generation (Supporting Information, Figure S20 and Table S5). Therefore, we believe that the freezing-induced force strongly depends not on the bonding state of the linkages, but on the coagulation of the swelling solvents.

The effects of weight swelling degree (Q) and melting (freezing) point of the swelling solvent on the freezing-induced color change are shown in the Supporting Information, Figure S21. The color change was observed in the gels swollen with solvents that have relatively high melting points and showed high swelling degrees. Therefore, we concluded that the linkages were cleaved in response to the mechanical force induced by coagulation of the solvents, when the solvent molecules sufficiently penetrated the networks and when the solvent coagulated at a higher temperature, that is, above 0 °C. Only a small force was generated along the polymer chains when the interactions between the chains and the solvent molecules were weak, and higher thermal energies were necessary to cleave the linkages at lower temperatures because of the increased stability of the linkages.

In conclusion, the present work demonstrated that DABBF derivatives could act as color-changing mechanophores and that freezing polymer gels induced force along polymer chains by means of incorporating DABBF into the chains. The radical system of DABBF revealed how much DABBF dissociated and how much mechanical energy was generated along polymer chains by the freezing-induced force, through EPR measurements. While it has been reported that freezing polymer solutions generates some kind of mechanical force along the chains and we found that cross-linking efficiently propagates the force through the chains, we can conclude that the force is not large enough to cleave usual covalent bonds. We believe that the natures of DABBF such as color changing, radical mechanism, and reversibility will elucidate other debated issues in the polymer field, leading to improve materials properties.

Keywords: cross-linked polymers · dynamic covalent chemistry · gels · mechanochemistry · mechanochromism

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