

On the Structure of Polymeric Composite of Metallocarborane with Poly(ethylene oxide)

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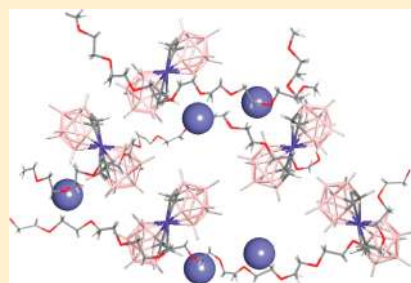
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 Supporting Information

ABSTRACT: We studied a structure of polymeric composite based on spontaneous precipitation of sodium [3-cobalt(III) bis(1,2-dicarbollide)], NaCoD, with poly(ethylene oxide), PEO, in salted aqueous solutions. Although the solid nanocomposite, which can be considered as a homogeneous matter, cannot form monocrystals due to the high flexibility of PEO chains, we can characterize the PEO/NaCoD structure by means of solid state NMR spectroscopy, from WAXS reflections and with help of already published structures of related systems. It indicates that the layered structure of solid NaCoD and the helical crystalline structure of PEO have disappeared after their mutual interaction. The NMR results clearly show that CoD⁻ anions are regularly dispersed within the PEO matrix, which consists of two distinct types of polymeric chains: one part interacting with dicarbollide clusters and the second one acting as a ligand of sodium counterions that also form regular pattern within the composite.



INTRODUCTION

Boron cluster compounds represent an attractive target for basic research and applications.^{1,2} Their importance for biomedical purposes is clearly reflected by a growing number of related papers appearing in recent years.^{3–7} As concerns their exploitation in macromolecular science, we will mention carboranes and metallocarboranes separately: Icosahedral carboranes are frequently used for preparation of high temperature resistant polymers,^{1,8} boron-containing macromolecules for boron neutron capture therapy, BNCT,^{8,9} and luminescent copolymers with a large system of conjugated electrons.^{10,11} Metallocarboranes, such as cobalt bis(dicarbollides), have been attracting an interest since their discovery by Hawthorne.¹² A vast number of papers deals with using of metallocarboranes as catalysts for polymerization of olefins.^{13,14} Cobalt bis(dicarbollides) can be successfully used as doping agents in conductive polymers for preparation of electrodes.^{15,16} Their unique structure manifests itself in possibility to form infinite polymer-like networks by themselves based on weak interactions.^{17–21} Another approach is to bind several charged boron clusters together via a covalent linkage.^{22–27}

Poly(ethylene oxide), PEO, has been widely used in medical applications mainly as component of drug delivery carriers.²⁸ Moreover, PEO-containing composites represent promising materials for solid-state electrolytes,^{29–31} devices exhibiting

nonlinear optical properties,³² and in general in composites where one combines the properties of soft polymeric material and an inorganic material for enhanced mechanical strength.^{33–35} For instance, clay/PEO nanocomposites can be interesting materials for rechargeable Li batteries.^{34,35} Polymer electrolytes consist of salts such as LiClO₄ and LiCF₃SO₃ that are dissolved in coordinating polymers like PEO.³⁶ For further progress in applications, it is crucial to understand a correlation of ion coordination and degree of PEO crystallinity with mechanical and electrical properties of such electrolytes.^{37–39} Further, PEO conformation in composites has been thoroughly studied upon addition of polymeric plasticizers, amino derivatives like urea, layered nanostructures, and nanoparticles in order to obtain materials with tunable properties.^{40–46} Of course, for all these purposes it is important to control the relations between microscopic structure and the macroscopic properties of the nanocomposites. In general, PEO is a rather interesting component for composite materials, once due to its polar character being variable depending on its chain conformation but even more so due its very biocompatible nature.

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Recently, we prepared a new polymeric material based on spontaneous precipitation of [3-cobalt(III) bis(1,2-dicarbollide)][−](−1) anion, CoD^- , with high-molar-mass PEO from salted aqueous solutions.⁴⁷ This rather unusual type of interaction could be exploited in preparation of drug-delivery systems suitable for metallacarborane-based drugs, which are potent inhibitors of HIV protease.⁴⁸ Further, PEO-based materials with dispersed hydrophobic anions like CoD^- could be also useful in designing novel solid electrolytes. Only little information is available on the inner structure of the composite. In this article, we focused on the assembly of cobalt bis(dicarbollide) within the polymeric composite by means of SAXS/WAXS and solid-state NMR and characterizing in addition this interaction thermodynamically by means of isothermal titration calorimetry (ITC). We studied almost exclusively the composite with “the equilibrium composition”. However, we carried out preliminary WAXS experiments with PEO/NaCoD films on glass substrates varying in the metallacarborane content (see Experimental Section). We believe that our study helps to understand what kinds of interaction are important for cobalt bis(dicarbollide) in the solid state and within the polymeric composite. This might open new opportunities in fabrication of nanostructured materials suitable for above-mentioned applications and open the pathway for new applications of metallacarboranes.

EXPERIMENTAL SECTION

Materials. The sodium salt of metallacarborane anion [3-cobalt(III) bis(1,2-dicarbollide)][−](−1), CoD^- , was a kind gift of Dr. Bohumír Grüner and Dr. Jaromír Plešek, Institute of Inorganic Chemistry, ASCR, Řež near Prague.⁴⁹ The water content in NaCoD hydrate was estimated by TGA to be 16 wt %.

The linear poly(ethylene oxide), PEO, was purchased from Fluka. It is characterized as follows: the weight-averaged relative molecular weights is 41.5×10^3 , and the polydispersity index is 1.10.

Preparation of Polymeric Composite. For the preparation a dialysis tube with aqueous solution of PEO was placed into a beaker with a large excess of NaCoD solution in 0.1 M NaCl. Further details on this procedure are given in ref 47. The precipitant of PEO/NaCoD was carefully removed from the dialysis tube, washed several times by water, and left to dry in a vacuum oven. A photograph of the composite is shown in the Supporting Information. Water content in the composite was estimated by TGA to be less than 0.5 wt %. It was also proven that the composite does not contain a measurable amount of NaCl, which is furthermore insoluble in a PEO matrix.

The samples for WAXS varying in PEO/NaCoD ratio were prepared as follows: Both PEO and NaCoD hydrate were dissolved in THF (80 and 400 mg/mL, respectively) and mixed together with PEO segment-per-metallacarborane ratio in the range 6–62. The thin films of PEO/NaCoD, PEO, and NaCoD formed on a glass substrate after the evaporation of THF. The overall weight of the film was about 20–40 mg. The samples were annealed overnight at 70 °C and left to dry in a high vacuum for 24 h.

Methods. *Wide-Angle X-ray Scattering (WAXS).* WAXS patterns were obtained using powder diffractometer HZG/4A (Freiberger Präzisionsmechanik GmbH, Freiberg) with Cu K α radiation ($\lambda = 0.1542$ nm, 40 kV, 45 mA, Ni filter) in the scattering angle range of 1.4°–40°, step size 0.1°.

Solid-State NMR Spectroscopy. All one-dimensional (¹H, ¹¹B, ¹³C, ²³Na MAS, and CP/MAS) and two-dimensional heteronuclear (¹H–X) and multiple-quantum (²³Na and ¹¹B MQ/MAS) NMR experiments were measured at 11.7 T using a Bruker Avance 500 WB/US NMR spectrometer in a double-resonance 4 mm and 2.5 mm probehead at

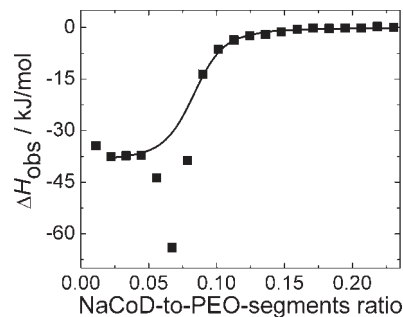


Figure 1. ITC thermogram for 0.0245 M NaCoD in 0.1 M NaCl titrated into 0.5 g/L PEO in 0.1 M NaCl showing both binding and “aggregation” (peak at 0.07) heats.

spinning frequencies 11 and 27 kHz, respectively. Detailed experimental parameters, schematic representation of the applied pulse sequences (Figure S1), and details of processing of MQ/MAS NMR spectra are given in the Supporting Information.

Isothermal Titration Calorimetry (ITC). ITC measurements were performed with an isothermal titration calorimeter (Nano ITC), TA Instruments - Waters LLC, New Castle, DE. The microcalorimeter consists of a reference cell and a sample cell (24 karat gold). The sample cell is connected to a 100 μL syringe. The syringe needle is equipped with a flattened, twisted paddle at the tip, which ensures continuous mixing of the solutions in the cell rotating at 200 rpm. Titrations were carried out by consecutive 5 μL injections of 24.5 mM NaCoD 0.1 M NaCl aqueous solution from the syringe into the sample cell filled with 960 μL of 0.5 g/L PEO 0.1 M NaCl aqueous solution. A total of 20 injections were performed with intervals of 1800 s. These injections replace a part of the solution in the sample volume, and the changed concentration is considered in the calculation of the sample concentration. By this method then the differential heat of mixing is determined for discrete changes of composition. The data were analyzed using the NanoAnalyze software.

RESULTS AND DISCUSSION

Poly(ethylene oxide), PEO, is molecularly soluble in water. The behavior of amphiphilic anion [3-cobalt(III) bis(1,2-dicarbollide)][−](−1), CoD^- , is peculiar in aqueous solutions.^{49–52} The metallacarborane precipitates with poly(ethylene oxide), PEO, in NaCl aqueous solutions due to the dihydrogen bonding of metallacarborane clusters with PEO and complexation of Na^+ counterions by polymer chains.⁴⁷

The interaction of PEO with NaCoD in water was studied by ITC (the thermogram shown in Figure 1; raw heat rate changes shown in Figure S2 of the Supporting Information): PEO solution in 0.1 M NaCl was titrated by 0.0245 M NaCoD solution. The PEO/NaCoD composite formation is exothermic with a sharp exothermic peak close to the point of saturation. This peak (ca. -27 kJ/mol) should not be likely related to the interaction heat, but to the splitting of CoD^- aggregates⁵² during a creation of the regular structure of the composite accompanied by its precipitation.⁵³ The isotherm was fitted by a simple one-site binding model (experimental points related to the aggregation peak were not included to the fitting procedure) with the parameters $\Delta H = -37.7$ kJ/mol and $\Delta G = -28.0$ kJ/mol and with the equilibrium composition ca. 12 PEO segments per one metallacarborane molecule. Strikingly, the experimental ΔG is almost identical to free interaction energy of PEO/ CoD^- pair calculated by quantum mechanics, and the PEO/NaCoD

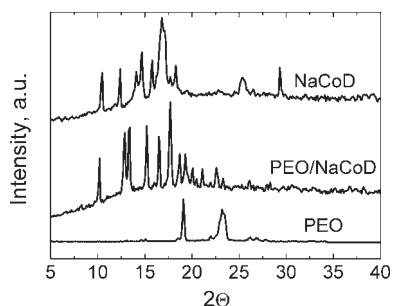


Figure 2. WAXS curves of PEO, NaCoD, and PEO/NaCoD composite.

composition is very close to ss-NMR and already published results.⁴⁷ These facts together with very slow titration rate (see raw heats in Figure S2) suggest that the process monitored by ITC correlates fairly well with the preparation protocol of the composite and its formation (slow dialysis). Furthermore, the state variables like ΔG should not in principle depend on the procedure of preparation as we assume that both systems (ITC and dialysis) reach the same state.

A question from our preceding paper⁴⁷ stands: whether the metallocarborane anions could be “molecularly” dispersed within the polymer matrix upon a formation of the composite. Therefore, we performed WAXS experiments to compare inner structures of parent compounds (PEO and NaCoD) with that of PEO/NaCoD. Solid high-molar-mass PEO contains crystalline domains as evidenced by typical WAXS peaks⁵⁴ shown in Figure 2. From their position and intensity (19.1° and 23.2°) we can assume a helical conformation^{55,56} with d -spacing equal to 4.64 and 3.83 Å. We should emphasize that no such crystalline domains were detected in PEO/NaCoD composite by WAXS as well as by additional DSC experiments and ss-NMR spectroscopy (see below). WAXS curves of NaCoD and PEO/NaCoD are worth noticing, suggesting that the composite has a unique organized structure as compared to parent NaCoD (Figure 2). We assume that NaCoD periodic structure resembles that of cesium salt (shown and described later).^{57,58} Nevertheless, it should exhibit a higher degree of disorder due to the presence of fluctuating amount of water in NaCoD hydrate. Interestingly, the TGA analysis of the PEO/NaCoD composite revealed that it does not contain almost any water molecules.

The composite cannot form monocrystals due to the presence of high-molar-mass PEO chains. Consequently, X-ray diffraction reflections that would allow determining precise atom positions were not obtained. Nevertheless, various unit cells were considered in the attempt to correlate the position of the reflections in the diffractogram (Figure 2) by using of the Rietveld refinement. At present, the monoclinic cell with $a = 11.578$ Å, $b = 14.088$ Å, $c = 16.998$ Å, and $\beta = 96.21^\circ$ seems to be the most favorable because ca. 10 corresponding reflections overlap with the experimental WAXS curve.

To obtain at least partial information on the structure of composites with “nonequilibrium” compositions, we carried out preliminary WAXS measurements of PEO/NaCoD films (see Experimental Section). The films of parent PEO and NaCoD exhibit almost identical reflections as the original samples. Unfortunately, the preparation procedure based on solvent evaporation of THF solutions does not lead to highly organized structures as observed in “equilibrium” composite (the samples

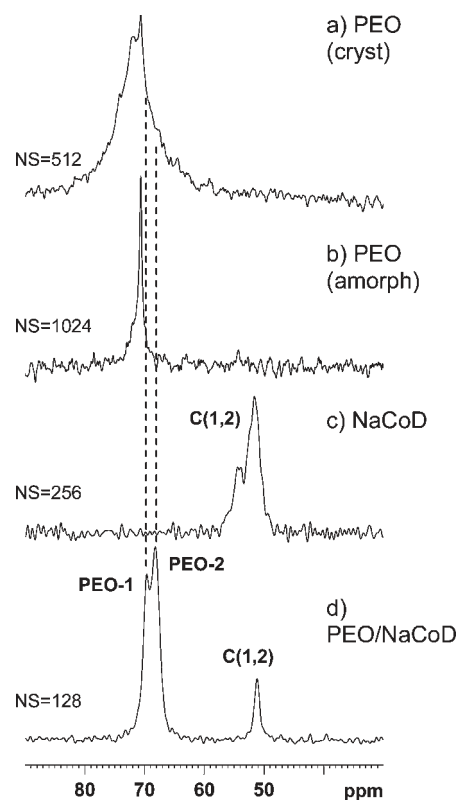


Figure 3. Domain-selective ^{13}C CP/MAS NMR spectra of (a) crystalline and (b) amorphous fraction of PEO detected in one polymer sample and standard ^{13}C CP/MAS NMR spectra of (c) NaCoD and (d) PEO/NaCoD composite. The number of scans (NS) is shown for each spectrum.

have not been further studied). However, we clearly observed the diminishing of reflections of crystalline PEO after addition of relatively low amount of NaCoD (ca. 2 times lower than “equilibrium” amount). It means that the presence of metallocarborane leads to reorientation of helically organized PEO chains into the amorphous phase. Nevertheless, the question we face is why the CoD^- clusters in samples prepared by THF evaporation are organized to such a low extent as compared to the spontaneously precipitated composite. We have no answer at the moment, and we will study samples differing in the composition, the procedure of preparation, and aging in our future research.

Solid-state NMR spectroscopy (ss-NMR) has long been a well-established method allowing to complement X-ray diffraction data and to get structural information on local arrangement in partially ordered systems.^{59,60} Especially for boron-cluster compounds, ^{11}B ss-NMR spectroscopy is obviously the most suited approach. Nevertheless, we found only few related examples of the application of this technique.^{61–63} In our particular case trying to obtain detail information on structure and segmental dynamics of the prepared material, we applied a wide range of ss-NMR experimental techniques covering traditional as well as advanced multidimensional approaches (for details see Supporting Information).

As reflected in ^{13}C CP/MAS NMR spectra (Figure 3), PEO chains as well as NaCoD assemblies undergo mutual self-organization processes when forming PEO/NaCoD composite: The broad signal of crystalline PEO (Figure 3a) completely

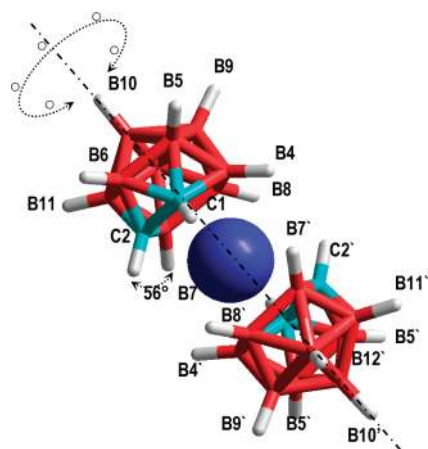


Figure 4. Schematic representation of the proposed 5-fold jump along B10–B10' axis between different positions of C and B atoms with C–H vector reorientation angle ca. 56° of [3-cobalt(III) bis(1,2-dicarbollide)][−] together with the numbering of BH and CH units. Color coding: H white, B red, C cyan, Co blue ball.

disappears. The narrow signal of amorphous PEO (Figure 3b) is slightly broadened, moved toward lower frequency, and split into two signals (68.0 and 69.5 ppm). Similarly, the asymmetrically broadened signal of CH_{1,2} units of pure NaCoD (Figure 3c) is dramatically narrowed in the composite (Figure 3d). The presence of a single line representing CH_{1,2} groups in the composite indicates high degree of local symmetry of CoD[−] clusters. This also indicates that considerable molecular disorder of metallacarborane clusters in the parent NaCoD system (presence of various rotamers or inconsistent molecular packing in crystal lattice) disappeared. This finding can be explained by the static uniform molecular arrangement of CoD[−] clusters in polymer matrix or by the enhanced segmental dynamics that motionally averages local structural motifs within the time window of NMR experiments. From the corresponding peak area in PEO/NaCoD spectrum (Figure 3d), we can estimate the PEO/NaCoD composition: the polymeric matrix consists of two distinct forms of PEO chains, PEO-1 (40%) and PEO-2 (60%), and the composite contains 14 PEO segments per one NaCoD molecule that is close to the value obtained by ITC.

Following these findings, we tried to obtain information on the dynamics of the polymer matrix analyzing the efficiency of ¹H–¹³C cross-polarization. It was striking that ¹³C CP/MAS NMR signals of PEO segments were easily created only for the composite system (low NS in Figure 3d), while the detection of the ¹³C CP/MAS NMR spectrum of pure amorphous PEO with acceptable signal-to-noise ratio required extensive signal accumulation (high NS in Figure 3b). It means that cross-polarization is nearly ineffective in pure PEO probably due to the high-amplitude segmental motions, while the presence of CoD[−] clusters in PEO matrix significantly hinders these motions, reestablishing thus suitable conditions for the effective cross-polarization transfer.

More profound information on segmental dynamics is usually provided by spin-relaxation experiments. However, the analysis of standard spin–lattice and spin–spin relaxation experiments in terms of motional frequencies is practically impossible for the system, in which multiple dipolar couplings involving many abundant and rare nuclei (¹H, ¹⁰B, ¹¹B, ²³Na, ¹³C) act simultaneously. Therefore, we applied alternative site-specific measurements of

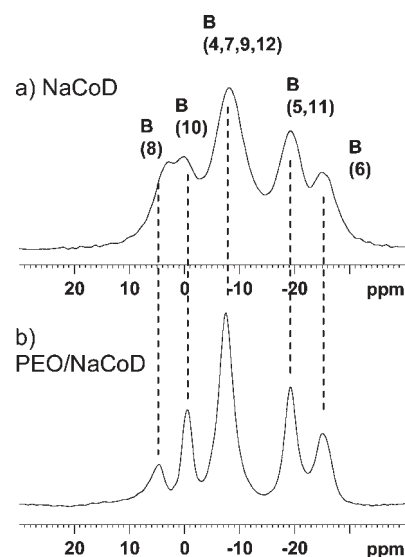


Figure 5. Solid-state ¹¹B MAS NMR spectra of (a) NaCoD and (b) PEO/NaCoD composite. For signal assignment see literature data in ref 67.

motionally averaged ¹H–¹³C one-bond dipolar couplings that carry information about motional amplitudes of molecular segments. In the next paragraph, we will briefly mention the most important results, and one can find further information as well as the dipolar profiles (Figure S3) in the Supporting Information or in refs 64–66.

The obtained dipolar profiles clearly reveal substantial differences in motional amplitudes of individual segments. Parent amorphous PEO chains exhibit nearly isotropic high-amplitude motion. On the other hand, PEO segments in PEO/NaCoD composite show significantly reduced motional amplitudes, where PEO-1 segments are a bit more mobile than PEO-2 ones. We can speculate that the PEO-2 signal represents the fraction of PEO interacting with the bulky metallacarborane cluster via several dihydrogen bonds, while the PEO-1 signal originates from the PEO chains involved in the complexation of Na⁺. On the basis of the composition data, 5–6 PEO segments coordinate Na⁺, and the rest (7–9 PEO segments) interacts with the metallacarborane cluster as related to one NaCoD molecule. Similarly, we found significant differences in the dynamics of CoD[−]. The clusters are rigid in pure NaCoD, while their molecular motion is dramatically enhanced in the polymer composite. Keeping in mind the rigid structure of metallacarborane clusters, where the rotation of both “hemispheres” along B10–B10' axis is the only possibility,⁶⁷ the motion of CoD[−] in the composite can be well explained by the 5-fold jump with C–H vector reorientation angle ca. 56° (schematic representation in Figure 4; further details in the Supporting Information). These fast jumps of CoD[−] within the PEO matrix was definitely confirmed by the measurements of ¹H–¹¹B cross-polarization rate constants *T*_{1S} (Figure S4; further details in the Supporting Information).

¹¹B MAS NMR spectra that are particularly suited to probe structure of boron-containing compounds then also showed significant differences in the arrangement of metallacarborane clusters in parent NaCoD and the corresponding PEO/NaCoD composite. Predominantly, one can see a clear narrowing of all ¹¹B NMR signals and a considerable shift of the signals of boron

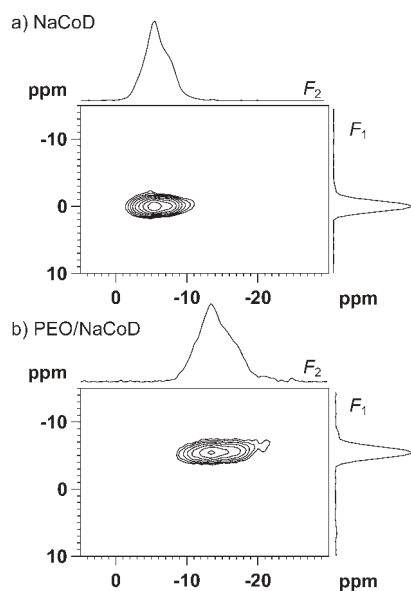


Figure 6. Two-dimensional ^{23}Na triple-quantum MAS NMR spectra of (a) NaCoD and (b) PEO/NaCoD composite.

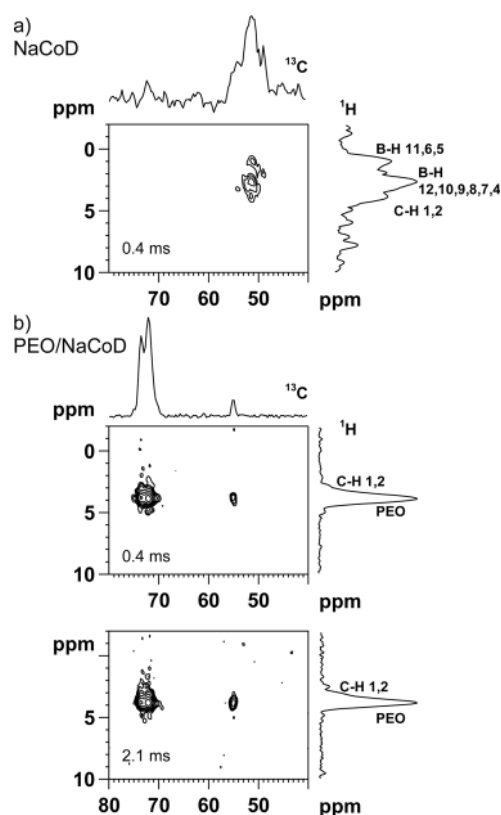


Figure 8. Solid-state ^1H – ^{13}C FSLG-HETCOR NMR spectra of (a) NaCoD and (b) PEO/NaCoD composite.

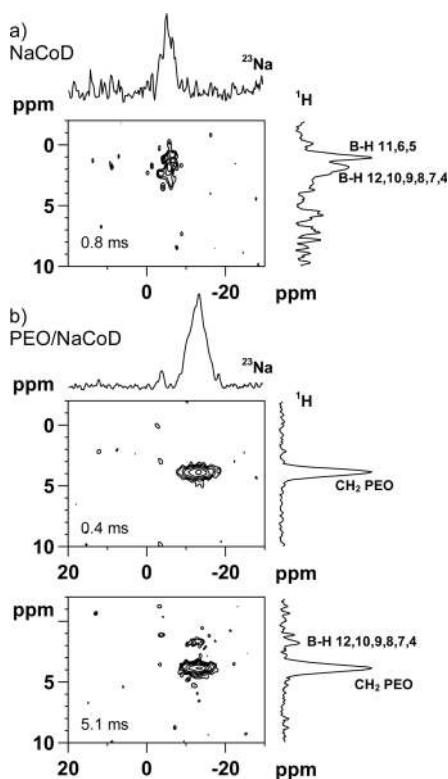


Figure 7. Solid-state ^1H – ^{23}Na FSLG-HETCOR NMR spectra of (a) NaCoD and (b) the corresponding PEO/NaCoD composite.

sites B8 and B10 in PEO/NaCoD (Figure 5). This indicates that local arrangement around these sites is considerably changed when built in the PEO matrix.

As follows from the recorded two-dimensional ^{11}B multiple quantum (MQ) MAS NMR spectra (Figures S5 and S6 in the Supporting Information), the dominant contribution to the

observed signal broadening in pure NaCoD system is the distribution of isotropic ^{11}B NMR chemical shift (further comments in the Supporting Information). The presence of at least two nonequivalent boron sites is indicated by a weak splitting of the B8 and B10 correlation signals. These findings clearly indicate that the dominant contribution of the broadening of the correlation signals of NaCoD system results from its structural disorder. As it has been mentioned, this disorder can result either from the presence of different rotamers of CoD^- , from the imperfect crystal packing, or from the presence of more than single symmetry independent clusters in the crystal unit. As concerns PEO/NaCoD, no considerable splitting or broadening of the correlation signals was observed. Thus, CoD^- clusters do not exhibit any significant molecular disorder as being uniformly dispersed within the PEO matrix forming the regular crystalline-like system (spectra in Figures S5 and S6 of the Supporting Information).

As indicated by the splitting of ^{13}C CP/MAS NMR signal of PEO, our considerations about global structure of PEO/NaCoD composite must include sodium ions. Similarly like ^{11}B nuclei, also sodium ^{23}Na is extremely receptive with 100% natural abundance, high gyromagnetic ratio, and spin $I = 3/2$. Consequently, solid-state ^{23}Na MAS NMR spectra have high potentiality to reflect chemical nature, coordination geometry, and dynamics of Na^+ . In our particular case the pure NaCoD is characterized by relatively narrow signal centered at ca. -5.5 ppm, while the signal of PEO/NaCoD is broadened and significantly shifted toward lower frequencies to ca. -13 ppm (Figure 6, F_2 projection; Figure S7 in the Supporting Information). As the observed broadening of the signal can be caused either by the

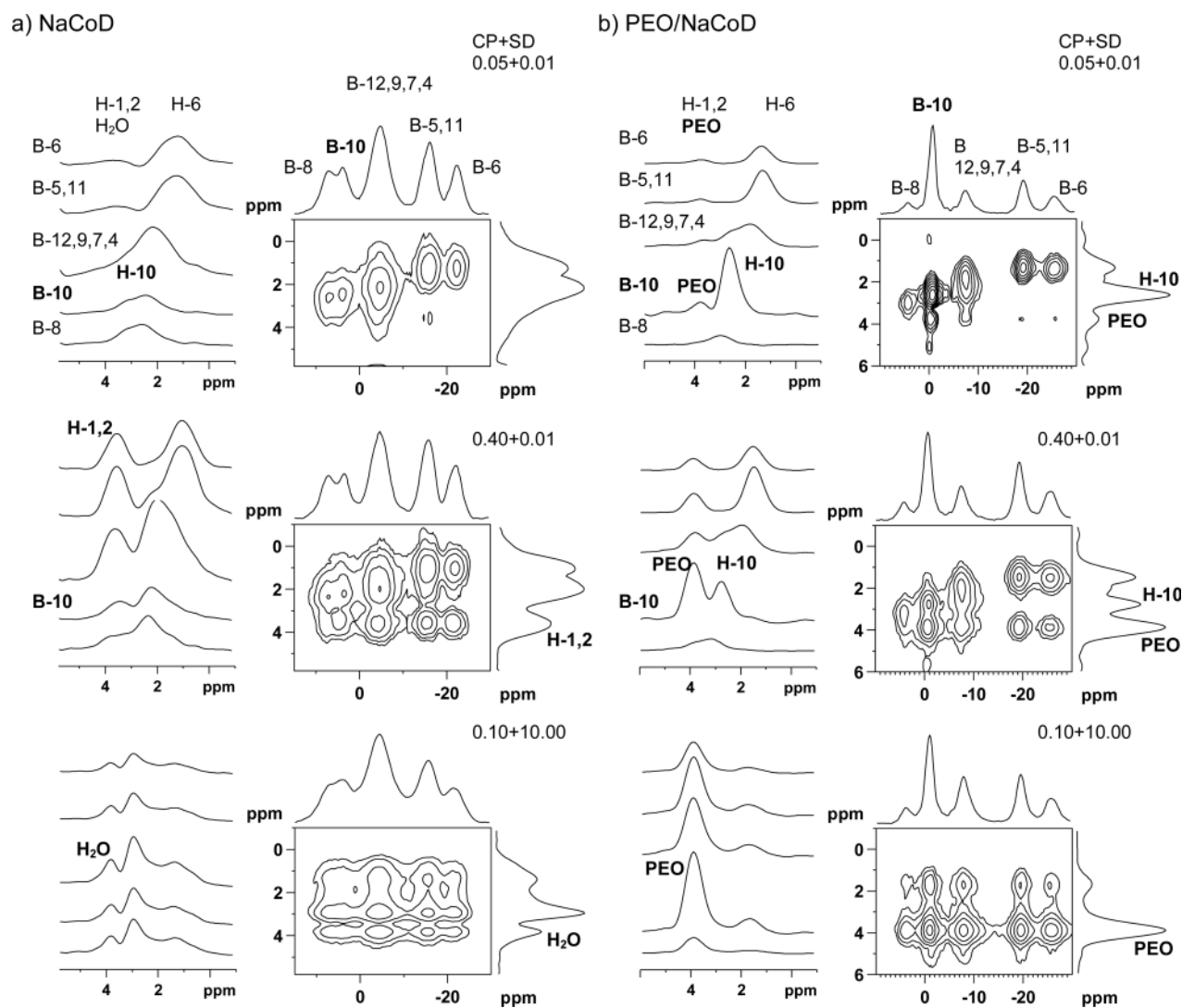


Figure 9. Solid-state ^1H – ^{11}B FSLG-HETCOR NMR spectra of (a) NaCoD and (b) PEO/NaCoD composite. The spectra were measured at various cross-polarization (CP) and spin-diffusion (SD) mixing times. Cross-polarization was systematically varied from 50 μs to 1 ms, while spin-diffusion mixing period from 100 μs to 20 ms. ^1H slices of every boron site are placed on the left side of each 2D spectrum.

increase in quadrupolar couplings (changes in coordination geometry) or by the increase in the distribution of chemical shifts (distribution of local structures involving Na^+), the 2D ^{23}Na triple-quantum MAS NMR spectra were recorded (Figure 6).

In both cases, relatively small quadrupolar coupling constants (see Table S1 in the Supporting Information) and the remarkably narrow F_1 projections of 2D spectra (half-width $\Delta\nu$ is ca. 2 ppm) indicate that sodium ions are rather symmetrically coordinated (in spherical octahedral or tetrahedral coordination) and uniformly arranged without a considerable structural disorder. This finding is somewhat in contrast with the previously observed substantial broadening of ^{13}C and ^{11}B MAS NMR signals of the pure NaCoD. This discrepancy can be explained by the effective separation of sodium ions from the disordered metallocarborane clusters in the NaCoD system. Sodium ions, probably forming sheets or channels, remain regularly arranged, adopting thus a high degree of spherical coordination symmetry. In contrast, the Na^+ coordination symmetry is a bit distorted in PEO/NaCoD. The observed broadening and a dramatic shift of

^{23}Na MAS NMR signal toward the low-frequency region indicate significant rearrangement and direct incorporation of sodium ions into the polymer matrix, in which oxygen atoms of PEO segments act as ligands.⁶⁸

To find the preferred positions of sodium ions in the studied metallocarborane systems, a series of ^1H – ^{23}Na cross-polarization (CP) and heteronuclear correlation (HETCOR) NMR experiments were performed. In this type of experiment the NMR signals are generated only if ^{23}Na nuclei are effectively coupled to nearby ^1H spins; i.e., the average ^1H – ^{23}Na distance is not larger than 4 Å, and both the nuclei are relatively rigid.

While in the case of the parent NaCoD system the ^1H – ^{23}Na cross-polarization was nearly ineffective requiring a very high number of signal accumulations and relatively long contact time (500 μs), in the case of PEO/NaCoD the CP efficacy was significantly higher (see Figure S8 in the Supporting Information). These differences are also reflected in ^1H – ^{23}Na FSLG HETCOR correlation spectra (Figure 7), in which NaCoD clusters in the parent system are characterized by a weak correlation signal that covers the entire ^1H frequency range expected for

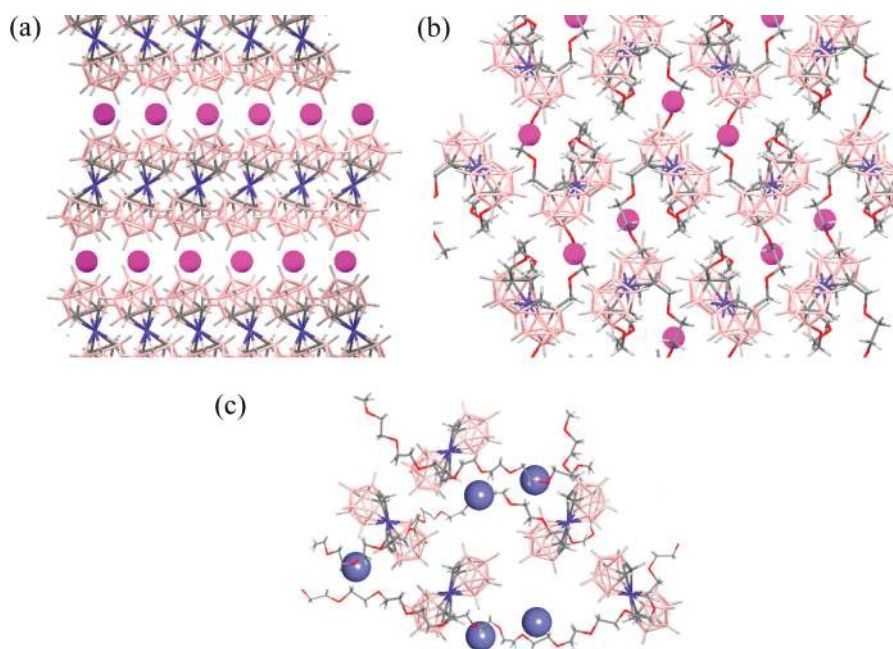


Figure 10. (a) $\text{Cs}[\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ and (b) $\text{Cs}[\text{Co}(1\text{-CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$ structures based on literature data (refs 57 and 69, respectively) and (c) the proposed structure of PEO/NaCoD composite. Color coding: B salmon, C gray, O red, H white, Co Blue, Cs pink balls, Na blue balls.

all C–H and B–H groups (ca. 4–0.5 ppm, Figure 7a). This confirms that sodium ions are rather isolated, forming large effectively separated lamellae or channels occupied also by highly mobile H_2O molecules.

In contrast, sodium ions in the NaCoD/PEO composite produce the strong correlation signal resonating at 3.7 ppm in ^1H dimension even after the short cross-polarization transfer (0.4 ms, Figure 7b). This confirms that Na^+ ions are fully and directly incorporated into the polymer matrix with the coordination slightly deviated from ideal spherical symmetry (quadrupolar coupling constant 1.8 MHz). Low-intensity correlation signals at 1.0 and 2.1 ppm appearing after the long cross-polarization confirm that CoD^- clusters are relatively far from sodium ions, which are preferentially located on the opposite side (signal at 2.1 ppm) than slightly positively charged $\text{CH}_{1,2}$ units.

The extent of incorporation of CoD^- clusters into the polymer matrix was extracted from ^1H – ^{13}C FSLG HETCOR NMR spectra (Figure 8; see also ^1H MAS NMR spectra in Figure S9 of the Supporting Information). Metallocarborane clusters in pure NaCoD system produce a broad ^1H correlation signal (nearly triplet) that reflects all B–H and C–H protons of the cluster involved in $^1\text{H} \rightarrow ^{13}\text{C}$ polarization transfer (Figure 8a). In contrast, CoD^- clusters in the composite are characterized by a single narrow ^1H correlation signal recorded both after short and long cross-polarization periods (Figure 8b). The position of this correlation signal in ^1H dimension is quite identical with the position of the correlation signal of PEO segments, indicating that PEO protons are effectively the only source of ^1H magnetization. This finding indicates very close mutual proximity and strong interactions between PEO and metallocarborane molecules. Therefore, we assume that CoD^- anions do not form any multimolecular domains (aggregates), but they are rather uniformly dispersed within the PEO matrix.

Solid-state ^1H – ^{11}B HETCOR spectra (Figure 9) then finally confirm the above-introduced structural assumptions. At first,

the narrow ^1H correlation signals resonating at ca. 4.0 ppm which appear in the NaCoD spectrum measured with rather long spin-diffusion period of 10 ms (Figure 9a, bottom spectrum) indicate water molecules that exhibit weak but still measurable interaction with CoD^- clusters. These H_2O molecules are incorporated into the molecular structure of NaCoD system filling some channels or sheets as proposed above. Second, one can see extraordinarily strong H10–B10 correlation signal in PEO/NaCoD after even a very short cross-polarization period (Figure 9b, upper spectrum, CP = 50 μs). It confirms uniaxial rotation (jumps) of CoD^- clusters, which only can preserve strong dipolar couplings in H10–B10 spin pair. In addition, at the same CP mixing time the B10 site exhibits clear correlation with PEO segments. Finally, in the correlation spectra of PEO/NaCoD system measured with a bit longer spin-diffusion periods starting from 400 μs (Figure S10 in Supporting Information and Figure 9b, bottom spectrum), PEO segments become dominating external sources of ^1H magnetization for the effective ^1H – ^{11}B cross-polarization. This perfectly shows that CoD^- clusters are regularly embedded within the PEO matrix and do not self-aggregate.

To estimate atom positions in the PEO/NaCoD periodic structure, we can take advantage from already published structures of cesium cobalt bis(carborane)⁵⁷ and its derivative with two $\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-}$ pending groups⁶⁹ (see Figure 10, a and b, respectively). CsCoD structure consists of layers of mutually interacting boron clusters intercalated by zones of Cs^+ . This motif has completely changed after the attachment of $\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-}$ groups with the affinity to alkaline cations via oxy groups. We are aware of differences between our systems and the published ones. NaCoD is a hydrate containing a substantial amount of water, which coordinates Na^+ . In contrast to the structure published by Chamberlin,⁶⁹ the composite is based on weak interactions.

When constructing the probable PEO/NaCoD structure (Figure 10c), we should take into account the following facts:

(i) CoD^- clusters do not form any multimolecular domains and the periodic position of CoD^- should be more similar to that of the cobalt bis(dicarbollide) derivative (Figure 10b) than CsCoD (Figure 10a), (ii) alkaline counterions do not form layered zones and they are complexed exclusively by PEO chains, and (iii) PEO does not form any crystalline domains and there are two distinct types of PEO segments: the first one is involved in dihydrogen bonding with CoD^- , and the second one forms the complex with Na^+ . As in the case of Cs/NaCoD structure, we should keep in mind that the image c of Figure 10 should be taken as the 2D static visualization of the 3D dynamic structure with rotating CoD^- and partly flexible PEO chains.

CONCLUSIONS

We studied the internal structure of polymeric composite based on spontaneous precipitation of sodium [3-cobalt(III) bis(1,2-dicarbollide)], NaCoD , with poly(ethylene oxide), PEO, in aqueous solutions. The interaction between NaCoD and PEO is exothermic at the given mixing conditions, and the composite formation is accompanied by a rearrangement of CoD^- aggregates in water into regular structure of the composite as evidenced by ITC. The PEO/ NaCoD composite as well as parent PEO and NaCoD was investigated by means of WAXS and various ss-NMR techniques.

The solid NaCoD consists of rigid (“frozen”) CoD^- clusters with significant degree of structural variability that originates from the presence of various rotamers or inconsistent molecular packing in the crystal lattice. Somehow independent layers or channels of Na^+ ions, which are coordinated by freely moving water, intercalate the regions of boron clusters.

The structure of PEO/ NaCoD composite is completely different as compared to the pure NaCoD . The CoD^- clusters are uniformly dispersed within the polymeric matrix with no evidence of multimolecular aggregates. Metallocarborane clusters can “freely” rotate along the $\text{B10}–\text{B10}'$ axis. The PEO matrix does not contain any crystalline polymeric domains, and there are two distinct types of PEO segments. The first one is involved in dihydrogen bonding with CoD^- , and the second one forms the complex with Na^+ . All the sodium counterions are located at the same type of interaction sites. They are effectively separated from the metallocarborane anions and significantly immobilized by PEO chains. The composite contains almost no water molecules as well as NaCl impurities. The proposed structure of PEO/ NaCoD based on WAXS, ss-NMR results, and published structures of related systems is shown in Figure 10c.

ASSOCIATED CONTENT

S Supporting Information. Further experimental details on ss-NMR, additional ss-NMR spectra, and raw ITC data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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