Propellants, Explosives, Pyrotechnics, Volume 43, Issue10, 2018, pp. 1023-1031
DOI: 10.1002/prep.201800137

Propellants, Explosives, Pyrotechnics

DOI: 10.1002/prep.201800137

Nitrated Cross-linked β-cyclodextrin Binders Exhibiting Low Glass Transition Tempratures

Federico Luppi[+],[a] Hamish Cavaye[+],[a] and Eleftheria Dossi[+]*[a]

Abstract: Polymeric binders such as β-cyclodextrins (βCDs) are used to bind with other constituents of energetic formulations and to prevent accidental ignition. One of the advantages of βCDs is the ability to tune their properties by chemical modification. Here, we synthesised nitrated cross-linked βCDs (βNCXCDs) to produce new binders for energetic formulations. The cross-linking of βCD with non-toxic triethylene glycol diglycidyl ether (TEGDGE, X=T) and poly(ethylene glycol) diglycidyl ethers (PEGDGE, X=P) yielded soft, water soluble oligomeric compounds (βCXCDs) which can improve the processability of energetic formulations and contribute to their desensitisation. When the PEGDGE cross-linker was used, lower glass transition temperatures were achieved, which extended the operative range of the βCPCD binder to −20 °C. The analogous nitrated systems (βNCXCDs) were therefore synthesised using a 1:1 (v/v) ratio of 98% sulfuric acid/100% nitric acid or 100% fuming nitric acid, increasing their solubility in acetone and tetrahydrofuran. The nitrated derivatives were characterised by decomposition temperatures (200 °C) and energies (up to 1750 J g^{-1}) comparable to nitrocellulose. Moreover, the glass transition of the inert βCXCDs at low temperatures (< 0 °C) was conserved in the corresponding nitrated βNCXCDs, ensuring the desensitisation of energetic compositions even at low temperatures. This is the first time that nitrated derivatives of βCD with glass transition temperatures below 0 °C have been reported, suggesting such derivatives could make suitable replacements for nitrocellulose and other binders in energetic formulations.

Keywords: cross-linked β-cyclodextrin · diglycidyl ethers · energetic binder · low T_g

1 Introduction

Synthetic and semi-synthetic polymeric binders are important components of most energetic formulations [1]. The role of the binder is to improve the overall mechanical properties of the formulation and to coat the energetic molecules, thus shielding them from accidental stimuli and environmental degradation. Nitrocellulose, produced by the nitration of natural cellulose, is the most frequently used semi-synthetic polymer in energetic formulations [1].

During the past three decades, cyclodextrins (CDs) have been introduced as energetic binders in a small number of studies because they are natural molecules with a composition similar to cellulose and they have useful molecular inclusion properties [1,2]. Typical CDs are cyclic compounds containing six, seven or eight sugar rings (α, β and γCDs, respectively) linked together via α-glycosidic bonds. They are particularly useful in the food, cosmetic and pharmaceutical industries because they form complexes within their toroidal cavities with a wide range of molecules [2]. The physical properties of the CDs can be tuned to satisfy specific applications such as shielding other molecules from external stimuli [2,3], which is important in explosive applications [4–5]. The availability of hydroxyl functional groups allows the functionalisation of the macrocycles to further tune their physicochemical properties [2,3].

The inclusion properties of βCD and γCD binders can lead to stabilisation of energetic molecules because these molecules have larger cavities than αCDs [3–5]. Furthermore, nitrated cyclodextrins (NCDs) have been developed as energetic components, although fully-nitrated cyclodextrins are sensitive to electrostatic discharge (ESD), e.g. βCD nitrated to 85% is sensitive to ESD ignition at 0.0125 J [6]. To reduce the ESD hazard, pre-functionalisation before nitration can be achieved using inert molecules as cross-linkers [7,8]. NCDs initially cross-linked with epichlorohydrin in NaOH, polyallylamine in KOH or isocyanate in DMSO, are less sensitive to ESD ignition at 0.1288 J [8], which is a 10-fold reduction in sensitivity. In contrast, longer inert cross-linkers such as poly(ethylene glycol) (PEG) have been used in CD systems for pharmaceutical applications, resulting in the formation of insoluble gels [9,10]. Water-

[a] *F. Luppi,[+] H. Cavaye,[+] E. Dossi[+]*
Centre for Defence Chemistry, Cranfield University, Defence Academy of United Kingdom, Shrivenham, SN6 8LA, UK
**e-mail: f.luppi@cranfield.ac.uk*
hamish.cavaye@stfc.ac.uk
e.dossi@cranfield.ac.uk

[+] *The manuscript was written with contributions from all authors. All authors have approved the final version of the manuscript.*

Supporting information for this article is available on the WWW under https://doi.org/10.1002/prep.201800137

soluble CD polymers were obtained when acyl chloride PEG derivatives were used [11] but to the best of our knowledge these derivatives have never been converted to nitrated derivatives.

One of the most important properties of binders in energetic formulations is the glass transition temperature (T_g), at which the rubbery binder becomes glassy and brittle. PEG-based cross-linkers are favoured for their low glass transition temperatures because this increases the operative temperature range within which the cross-linked materials can successfully contribute as a binder [12] and desensitise the energetic formulation. The replacement of highly toxic cross-linkers with non-toxic materials is one of the requirements for new energetic formulations. The REACH regulation of the European Union, has introduced restrictions on the usage of certain isocyanates to improve the protection of human health and the environment from the risks that can be posed by chemicals [13,14]. In this context, the use of CDs and non-toxic ethylene glycol diglycidyl ethers ensures relatively mild and environmentally sustainable cross-linking conditions: CDs are obtained from natural and sustainable sources, water is used as the reaction solvent, and the reaction temperatures are kept low. The formation of stable ether linkages (C–O–C) between CDs and the diglycidyl ethers also supports further functionalisation such as the nitration of the cross-linked cyclodextrins (CXCDs). Several nitration methods for pure or cross-linked CDs have been reported, ranging from pure nitric acid or nitric/sulfuric acid mixtures to stronger and more advanced systems such as nitration in liquid CO_2 with nitrogen pentoxide [8,15]. The latest methods achieve full nitration whereas earlier methods resulted in up to 90% nitration of the available hydroxyl groups [15]. The complexation of explosive molecules in the CD cavities also reduces the sensitivity of the explosive to external stimuli [8].

Here we report the synthesis of a βCXCD system and its nitrated derivative βNCXCD using TEGDGE and PEGDGE cross-linkers. The two cross-linkers were chosen as soft segments for their low glass transition temperatures of −80 and −68 °C, respectively [16,17]. We selected βCD for the initial tests because it is less expensive than γCD. However, the γCD cavity would encapsulate larger energetic molecules and more tests using γCD will be published in the future. All βCXCDs were subsequently nitrated to determine the impact of the βNCXCD systems on degradation energies and the glass transition temperature. We also carried out preliminary studies to determine the degree of compatibility between the inert and nitrated products and energetic fillers.

2 Experimental Section

2.1 Materials

The βCD (≥97%, Sigma-Aldrich) was used from stock (TGA, 13% water content). Polyethylene glycol diglycidyl ether (PEGDGE 500 Mw, Sigma-Aldrich), ethylene glycol diglycidyl ether (EGDGE 174.2 g/mol, TCI Chemicals), sodium hydroxide (Fisher Chemicals), acetylated dialysis membrane (2000 MWCO, Sigma-Aldrich), tetra-n-butylammonium bromide (TBAB, Sigma-Aldrich), and triethylene glycol (TEG, Sigma-Aldrich) were obtained from commercial sources and used without further purification. Triethylene glycol diglycidyl ether (TEGDGE, 262.0 g/mol) was synthesised as previously described [14]. The βCXCD cross-linking ratio was determined by ^{1}H NMR.

2.2 Characterisation

NMR spectra were recorded on a Bruker Ascend (400 MHz) with a BBFO probe in deuterated dimethyl sulfoxide (DMSO-d_6) solution using tetramethylsilane (TMS) as an internal reference. Spectra were also recorded in deuterated water (D_2O) with 3-(trimethylsilyl)-1-propane-sulfonic acid sodium salt as an internal reference. Peak multiplicities were described as follows: singlet (s), doublet (d), triplet (t), multiplet (m), doublet of doublet (dd), and broad (br). Thermal properties were determined by DSC using a Mettler Toledo DSC822 or DSC30 with heating and cooling rates of 10 °C min^{-1} and a flow of dry nitrogen. The reported values were the measurements performed on samples with a mean weight of 10 mg for inert materials and low temperature, whereas 1 mg was used to assess the decomposition temperature of energetic materials. Yields were measured as mass of products over mass of reactants. Gel Permeation Chromatography (GPC) measurements were performed in tetrahydrofuran (THF) at 35 °C, using Agilent PLgel 10 μm mixed B columns and Agilent polystyrene calibration kit (M_w 500–6.9 × 10^6).

2.3 Synthesis of βCXCDs

The βCD (5–5.6 g, 3.8–4.4 mmol) was dissolved in 5.6–50% w/w NaOH (21.0 mL) and stirred mechanically for 0–16 h. Diepoxide (EGDGE n = 1, TEGDGE n = 3 or PEGDGE n = 9) (17.4–5.8 mL, 13.2–36.9 mmol) was then added dropwise in 20 min with vigorous stirring. The reaction mixture was heated to 30–70 °C for 30 min with vigorous stirring. After cooling for 20 min, the mixture was neutralised with 6 M HCl. The purification method depended on the solubility of the product in water. The volume of solvent for soluble products was reduced and the crude solute was precipitated in acetone three times. The solid was then collected and dissolved in distilled water and dialysed against

water using a cellulose membrane (2000 MWCO) for 5 days. The insoluble products were filtered from the crude reaction mixture and washed with acetone. The insoluble solid was then collected and suspended in distilled water and dialysed against water using a cellulose membrane (2000 MWCO) for 5 days. The dialysis water was replaced every day. The dialysed solid was collected and the water was evaporated under reduced pressure. The final product was characterised by ^{1}H NMR and DSC. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 5.9–5.6 (br m, O<u>H</u>–C_2, O<u>H</u>-C_3), 5.1-4.8 (m, <u>H</u>-1), 4.7-4.5 (br m, O<u>H</u>$_A$, O<u>H</u>$_B$ and O<u>H</u>$_C$), 4.4 (br m, O<u>H</u>–C_6), 4.0-3.2 (br m, βCD–OC<u>H</u>$_2$–(C<u>H</u>–O<u>H</u>)–C<u>H</u>$_2$–O–C<u>H</u>$_2$–C<u>H</u>$_2$). DSC (10 °C min^{-1}, N_2) 240–250 °C (dec) (See Supporting Information).

2.4 Synthesis of βNCXCDs

Nitric acid (95–100% 0.5–1 mL) or 100% nitric acid/100% sulfuric acid mixture (50:50 v/v, 1 mL) was poured into a round-bottomed flask and cooled to below 10 °C in ice water. Dichloromethane (DCM) (1.8 mL) was added when route 2 (Figure 2) was followed. The bath was removed and βCXCD (X = P and T, 200.0 mg) was added in small fractions over 5 min, ensuring that the temperature remained below 10 °C. The crude slurry or solution was then left stirring at room temperature for 1 h. The reaction mixture was poured into ice/water (10 mL) and the solid was dissolved in acetone (5 mL) and precipitated in water (100 mL). The clean product was collected, dissolved in acetone and dried under vacuum. Small portions necessary for characterisation were taken and the rest was stored under DCM. The ^{1}H NMR analysis was performed in acetone-d_6 and DMSO-d_6. DSC (10 °C min^{-1}, N_2) 197–210 °C (dec) (See Supporting Information).

3 Results and Discussion

3.1 Synthesis of βCXCDs

Several βCXCDs were synthesised at 70 °C to determine the effect of different parameters on the yield of the reaction and the physicochemical properties of the products. The cross-linked compounds were recovered after cooling the reaction mixture followed by neutralisation with 6 M HCl. The final products were obtained by precipitation from water in acetone followed by dialysis against water using a cellulose membrane with a molecular weight cut-off (MWCO) of 2000 for 5 days.

The cross-linking reaction involved the alkoxidation of βCD combined with diglycidyl ethers of two different lengths: PEGDGE with n = 9 repeating ethylene glycol units and TEGDGE with n = 3 ethylene glycol units. The hydroxide (OH^-) ions from the basic medium (NaOH) reacted first with the hydroxyl groups of the βCDs to form alkoxides, and the latter then reacted with the epoxide ring of the diglycidyl ether molecule. The hydroxyl groups of the βCDs would not react at room temperature with the epoxides. Heating the reaction mixture (up to 70 °C) under variable basic conditions (5.6% w/w, 40% w/w and 50% w/w) led to the partial substitution of all three hydroxyl groups attached to C-2, C-3 and C-6 atoms of βCD units in βCXCDs as from ^{1}H-NMR characterisation in dimethylsulfoxide (DMSO); this is discussed later in this paper. As a general rule for the reactivity of βCD hydroxyl groups, the primary hydroxyl groups attached to C-6 atom (Figure 1), are considered the most reactive [18–20]. The difference of reactivity of the primary and secondary hydroxyl groups of βCD cannot be assessed by the authors in these earlier studies due to the overlap of the hydroxyl proton signals in the NMR analyses. The number of unreacted hydroxyl groups attached to C-2 and C-3 atoms was evaluated by ^{1}H-NMR spectroscopy in dimethylsulfoxide (DMSO) and was found to depend on the concentration of NaOH. The least concentrated NaOH solution (5.6% w/w) promoted more cross-linkages whereas stronger NaOH solutions (40–50% w/w) inhibited the formation of the cross-linked product (Table 1) because of i) the higher amount of degraded cross-linker by the reaction conditions discussed in the following paragraph and ii) the supressed formation of βCD-alkoxide in the very viscous reaction mixtures.

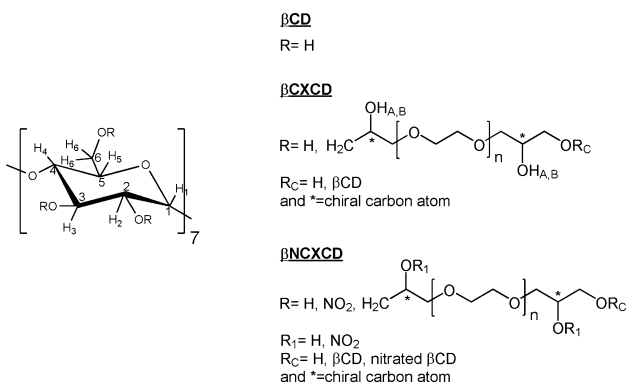

Figure 1. Proposed chemical structure of βCD, βCXCD and βNCXCD (X=T,P) with numbered H and C atoms.

Table 1. Effect of NaOH concentration on the properties of βCPCDs.

Sample[1]	NaOH[2] (% w/w)	Reaction time (h)	Yield[3] (%)	T_g (°C)	Water solubility
βCPCD1	50.0	1.00	< 1	–	Y
βCPCD2	40.0	1.00	< 1	–	Y
βCPCD3	5.6	0.66	88	−30	N

[1] PEGDGE:βCD ratio = 9:1, [2] Reaction temperature = 70 °C, [3] Yield measured as mass of products/mass of reactants.

Under the basic cross-linking conditions we used, a competitive side reaction occurs and the degradation of the diepoxide cross-linker produces a tetra-hydroxyl by-product, thus affecting the yield of the reaction and physical properties of the final product. The effect of the NaOH concentration was investigated at 70 °C for short reaction times (≤ 1 h) (Table 1) and this had a significant influence on the reaction. When the NaOH concentration was low, the reaction become more efficient and reached the gelation point accompanied by the appearance of a solid product and the increasing of the viscosity of the reaction mixture, whereas strong NaOH solutions delayed the formation of gels and affected the yield of the reaction due to faster cross-linker degradation.

We also investigated the effect of the number of ethylene glycol units in the cross-linker when the cross-linker:βCD ratio was maintained at 9:1, and 40% w/w NaOH was used for all the reactions. The trend of the reactions suggested that TEGDGE produces gels more quickly than PEGDGE. Given this result and the insoluble nature of the gels produced with TEGDGE, we decided to focus on the longer cross-linker (PEGDGE), which was expected to confer better mechanical properties upon the cross-linked products.

Another parameter that affects the cross-linking of βCD is the time needed to prepare its alkoxide. Initial trials suggested that leaving the βCD stirring in basic conditions for 16 h leads to better yields of soluble products (Table 2). It is therefore necessary to allow the cyclodextrin to form the alkoxidic groups prior to the addition of the cross-linker as discussed below. Indeed, the alkoxide promoted successful ether linkage formation between cyclodextrin and PEGDGE (see the Supporting Information).

Table 2. Role of the temperature on the yield of βCPCDs.

Sample	T (°C)	Yield (%)	T_g (°C)	Water solubility
βCPCD4[1]	70	1	–	Y
βCPCD5[1]	50	13	+6	Y
βCPCD6[2]	50	30	−18	Y
βCPCD7[2]	30	33	−22	Y

[1] Cross-linker:βCD = 5:1, 0 h alkoxide formation, 5 h reaction time,
[2] Cross-linker:βCD = 5:1, 16 h alkoxide formation, 5 h reaction time.

Higher temperatures affect the kinetics of cross-linking by increasing the rate of cross-linking and also by accelerating the degradation of the cross-linker. Two sets of trials were carried out using the following conditions: a low concentration of NaOH (5.6% w/w), a cross-linker:βCD ratio of 5:1, 0 or 16 h for the formation of the alkoxide and 5 h for the cross-linking reaction itself. The longer time for alkoxide formation was set at 16 h based on the results discussed above. The cross-linker:βCD ratio was set to 5:1 to prevent gelation, which occurred at the higher ratio of 9:1. The data summarised in Table 2 suggest that the cross-linker is more stable at 30 °C, but higher temperatures such as 50 °C and 70 °C reduce the yield due to the loss of cross-linker in the competitive degradation reaction.

The effect of the cross-linker:βCD ratio was investigated under the optimal conditions determined thus far, i.e. 5.6% w/w NaOH, 30 °C, 16 h for the formation of the alkoxide and 5 h for the completed cross-linking reaction (Table 3). The thermal properties of the cross-linked products at low temperatures were affected, i.e. lower amounts of cross-linker resulted in products with higher degree of crystallinity and higher T_g. The ratio of cross-linker:βCD in the cross-linked product is lower than in the initial feed of the reaction. The difference is caused by the degradation of the cross-linker as mentioned above and the NMR analysis of the compounds is discussed in detail later, in the section dealing with characterisation.

Table 3. Effect of cross-linker:βCD ratio on the properties of βCPCDs.

Sample[1]	Cross-linker:βCD ratio feed	Cross-linker:βCD ratio by NMR	Yield (%)	T_g (°C)	Water solubility
βCPCD7	5:1	3.75:1	34	−22	Y
βCPCD8	4:1	3:1	36	−13	Y
βCPCD9	3:1	2.25:1	68	−3	Y
βCPCD10	2:1	1.5:1	44	+8	Y

[1] 5.6% (w/w) NaOH, 30 °C, 16 h alkoxide formation, 5 h reaction time.

A final investigation demonstrated that the duration of the addition of the cross-linker to the reaction mixture also influenced the reaction yield. If prolonged addition times were used, a small proportion of cross-linker was lost in the competing degradation reaction. Further studies are needed to determine the optimal conditions to improve the yield of water-soluble samples (≤ 68% at present). Higher yields were achieved only for insoluble gels. The cross-linking of βCPCDs therefore requires further optimisation. The samples obtained in these early experiments were used for the nitration reactions described in the following section.

The images of βCPCD7 and its precursor βCD were compared by scanning electron microscopy (SEM) and the corresponding images are provided in the Supporting Information. The images show the homogeneity of the surface of the βCPCDs, whereas the βCDs have a crystalline appearance.

3.2 Synthesis of βNCXCDs

The βCXCDs were functionalised with nitro groups to form energetic derivatives that can contribute energy to explosive formulations. The nitration of a set of water-soluble

βCPCDs and insoluble βCTCD precursors with variable physical properties was carried out using the reaction conditions shown in Figure 2.

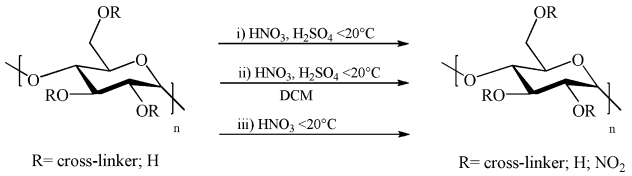

Figure 2. Overview of the synthesis of βNCXCDs.

In initial tests we evaluated the following nitration methods: (i) using 1:1 98% sulfuric acid/100% nitric acid; (ii) two-phase nitration, using 1:1 98% sulfuric acid/100% nitric acid followed by dichloromethane (DCM); and (iii) using 100% fuming nitric acid as the nitrating phase. DCM did not improve the control and/or efficiency of the nitration reaction because the βNCXCDs were insoluble in DCM and were not extracted from the acidic water phase during the reaction. Therefore, DCM was not included in subsequent experiments. Attempts to nitrate insoluble gel compounds also achieved no control of the nitration reaction, and thus the physicochemical and hazard properties of the products were unpredictable, so these precursors were also abandoned.

The βCXCDs were difficult to dissolve in the mixed acids and their conversion to analogous nitrated products was compromised. The sulfate esters [21,22] of βCXCDs formed in these nitration conditions are expected to affect their solubility and consequently the efficiency of the nitration reaction. In contrast, the βCXCDs dissolved efficiently in the fuming nitric acid within the 1-h duration of the nitration reaction. Table 4 summarises the data obtained when 100% fuming nitric acid was used as the nitrating agent. All βNCPCDs were soluble in organic solvents such as acetone and THF, suggesting good processability, which is important in energetic formulations because the different components must be mixed thoroughly. The βNCPCDs were purified by re-precipitation from acetone in water and their thermal stability was satisfactory, as shown by their high decomposition energy and negative T_g values. A nitrated sample βNCPCD1 was examined by gel permeation chromatography (GPC) in THF and compared with poly(styrene) standards. The results Mn = 7350 Da and Mw = 15140 Da, confirmed the polymeric nature of the sample (see Supporting Information).

Like the βCPCDs precursors, the T_g of the nitrated products was dependent on the number of soft ethylene glycol units in the cross-linker. The T_g increased when less PEGDGE was used (Table 4) and we speculate from very preliminary modelling [23] investigation on nitrated CDs that the polar nitro groups could inhibit the mobility of the polymeric chains. On the other hand, the large number of OH to ONO_2 (nitrato) transformations contributed to the overall energy of the system. The decomposition temperature (T_{dec}) stabilised at 196 °C, which is similar to nitrocellulose samples with a 12.5% nitrogen content [24]. As expected, the energy of the system was also affected, with higher decomposition energies (ΔH_{dec}) such as 1750 J g^{-1} for sample βNCPCD3. The thermal properties of the βNCPCDs can be tuned to give the desired product for specific applications. A very small, second-order transition was observed in all thermograms at ~80 °C, which was attributed to the glass transition of the rigid βCD units in the cross-linked systems.

When TEGDGE was used as the cross-linker, both the βCTCD precursors and the βNCTCDs derivatives were insoluble gels. The βNCTCDs were characterised by low T_g values, thermal stability and relatively low decomposition energies compared to the analogous βNCPCDs (Table 4). Although the cross-linker:βCD ratio was 9:1 to guarantee low transition temperatures, the degree of nitration was lower in these materials due to the inability of the acids to penetrate the polymer structure and efficiently nitrate the hydroxyl groups of the βCD units. The nitration of the same βCTCD resulted in the synthesis of βNCTCDs with variable properties. This highlights the lack of control over the nitration of insoluble products. Also, it was difficult to purify the insoluble βNCTCDs from the acid traces. The stability of these products and their hazard properties is strongly affected by the efficiency of the purification process.

Table 4. Thermal properties of βNCXCD oligomers.

Nitrated sample[1]	Precursor Name	cross-linker:βCD	Reaction time (h)	T_g (°C)	T_{dec} (°C)	ΔH_{dec} (J g^{-1})
βNCPCD1	βCPCD7	5:1	1.0	−20	202	1500
βNCPCD2	βCPCD8	4:1	1.0	14[2]	197	1640
βNCPCD3	βCPCD9	3:1	1.0	19	199	1750
βNCTCD1	βCTCD1	9:1	1.0	−21	210	530
βNCTCD2	βCTCD1	9:1	1.0	−20	208	650

[1] Using 200 mg of precursor and 1 mL 100% HNO_3, [2] Very broad transition; more investigation needed.

3.3 Chemical Characterisation

The cross-linked products we synthesised were characterised by ^{1}H NMR spectroscopy in deuterated dimethylsulfoxide (DMSO-d_6) and deuterated water (D_2O) as solvents. DMSO-d_6 was used to investigate the reactivity of the hydroxyl groups of the βCDs at 4.4–5.5 ppm (Figure 3 and 4).

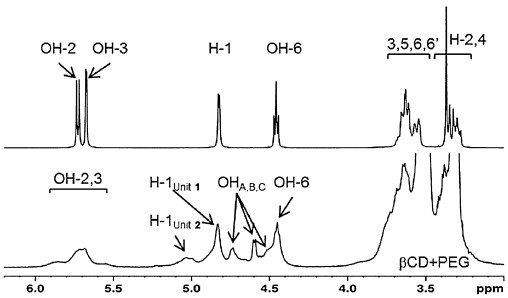

Figure 3. ^{1}H NMR spectrum of βCD and βCPCD8 in DMSO-d_6, suggesting the assignment of the proton of the OR groups when no substitution occurs. The OH_C assignment is expected when $R_1 = H$.

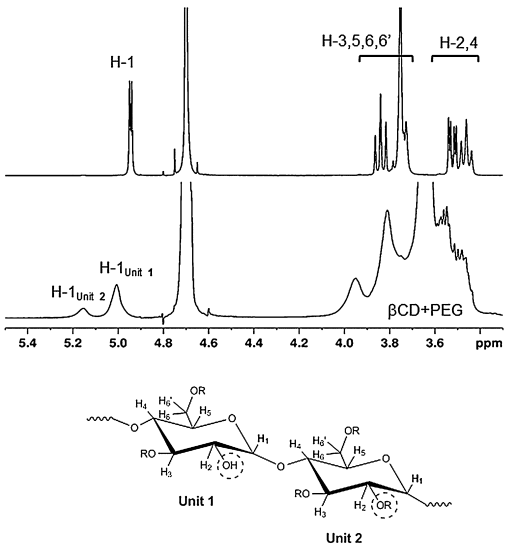

Figure 4. ^{1}H-NMR spectra of βCD (top) and βCPCD8 (bottom) in D_2O.

The spectrum of the βCPCDs shows broadened peaks due to the larger cross-linked molecules, when compared to the spectrum of pure βCD [2]. New peaks appear in the spectrum (Figure 4) and are attributed to the three hydroxyl groups (OH_A, OH_B and OH_C when $R_C = H$) on the cross-linking units. Due to the similar environments in the compound, many signals overlap. The water peak which overlaps the signals of the product at 3.3–3.4 ppm in DMSO-d_6 moves in the hydrogen-deuterium oxide (HDO) when D_2O is used, allowing us to determine the cross-linking ratio as reported below.

The cross-linker:βCD ratio in βCPCDs was calculated [11] from the ^{1}H NMR in D_2O (Figure 4).

- Integral 1 at 4.8–5.1 ppm = $n_{βCD}$ H-1 protons
- Integral 2 at 3.2–4.0 ppm = $6n_{βCD}$ H-2 to H-6 protons + $44n_{cross\text{-}linker}$ protons

The results show that the cross-linker is not consumed in the competing degradation reaction at 30 °C, allowing the reactants to react in a quasi-stoichiometric manner (25 % lower than the anticipated theoretical value, Table 3).

The βNCTCDs and βNCPCDs were characterised by ^{1}H NMR in acetone-d_6 and DMSO-d_6. The spectra recorded in DMSO-d_6 were compared with those of the starting oligomers and with a sample of nitrated βCD (βNCD) synthesised under the same conditions [15]. Figure 5 shows the ^{1}H NMR spectra of βNCD and βNCXCD in DMSO-d_6.

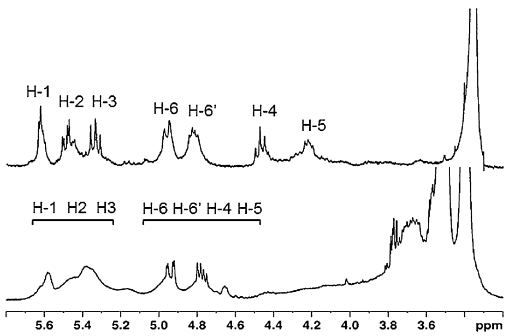

Figure 5. ^{1}H NMR spectra of βNCD (top) and βNCPCD1 (bottom) in DMSO-d_6. In the βNCPCD1 spectrum (bottom), the signals near the water peak are assigned to protons that are not near the nitrato groups.

The βNCPCD1 signals were broader due to the polymeric nature of this product. The broadness of the peaks and the down field shift of the signals compared to βCPCD reflect the complex chemical environment present in this energetic polymer. The different degrees of nitration on the cyclodextrin units result in overlapping signals representing protons close to the nitrato groups. The reference peak of proton H-1 close to the glycoside bond is present at 5.60 ppm. The broad signals at 5.55–5.10 ppm can be assigned to protons H-2 and H-3 attached to asymmetric carbon atoms 2 and 3, whereas the signals at 5.10–4.60 ppm can be assigned to CH_2, which is adjacent to nitrato groups in both βCD and the cross-linker units. Finally, the signals at 4.6–4.0 ppm can be assigned to CH_2 protons belonging to both βCD and the cross-linker units that are not adjacent to a nitrato group, but close enough to be influenced by them. The signals between 3.8 ppm and 3.2 ppm can be assigned to the methylene of the ethylene glycol units which are farthest from and least affected by the nitrato groups.

The degree of nitration in βNCD was determined using a previously described analytical method [15] and was nearly 90 %. The degree of nitration in the βNCPCDs will be as-

sessed in future studies based on iron sulfate titration and comparison with ion chromatography data.

3.4 Thermal Characterisation

The T_g of the βCXCDs and βNCXCDs was determined by differential scanning calorimetry (DSC) within the temperature range −100 °C to 100 °C at 10 °C min^{-1} and the results are reported in Tables 1–4. The T_g of the βCXCDs ranged between −22 °C and +8 °C and increased in line with the proportion of βCD because the cross-linker introduces more mobility into the system. The glass transitions reported for a similar cross-linked system based on a carboxylic acid PEG linker ranged from −20 °C to −16 °C [11]. These values are consistent with the properties gained by the cross-linked system studied herein.

The low T_g of the βCXCD precursors was transferred to the βNCXCD derivatives and ranged from −20 °C to +19 °C (Table 4). This transition is particularly wide compared to the non-nitrated precursor (Figure 6) and the material begins to soften at very low temperatures. The T_g midpoint is difficult to determine in the nitrated product due to the broadness of the transition, which may reflect the sum of different arrangements of the entangled cross-linker chains in the compound. Dynamic mechanical analysis (DMA) of βCXCD and βNCXCD samples is currently underway and the results will be published in a separate article.

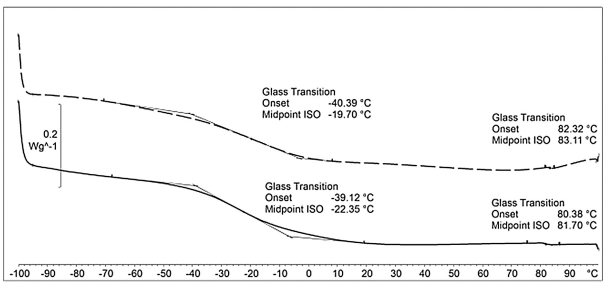

Figure 6. DSC thermogram of the glass transition of βCPCD8 (solid line) and βNCPCD1 (dashed line) between −100 °C and 100 °C.

All βNCPCDs derived from water-soluble βCPCD precursors showed similar thermal stabilities, with decomposition occurring at ~200 °C. This is comparable with the decomposition of nitrocellulose [24]. The decomposition energy fell within the range 1500–1750 J g^{-1} (Figure 7).

The energy released by the βNCXCDs was similar to that released by nitrocellulose samples with a nitrogen content of 12.5%, measured using the same method [24]. As expected, cross-linking affected the maximum nitrogen content of the βNCXCDs, which declined with the increasing content of inert ethylene glycol chains. DSC revealed that the βNCXCD systems displayed lower decomposition energies than the βNCD sample with 90% nitration

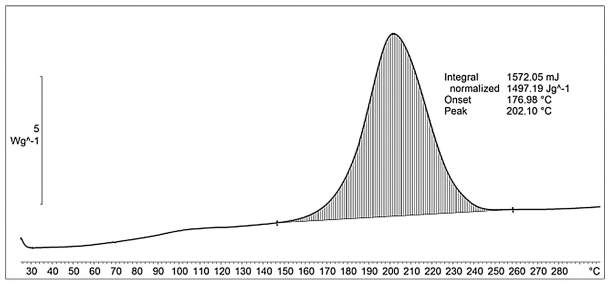

Figure 7. DSC thermogram of the decomposition of βNCPCD1.

(1880 J g^{-1}). Micro-calorimetry measurements will be performed in the future to measure the decomposition energy of the βNCXCDs and the effective release of energy from these systems.

The attempted nitration of insoluble βCXCD products also yielded compounds with a decomposition event at ~200 °C, but the decomposition energy was 500–800 J g^{-1}. This reduction in energy probably reflects the presence of fewer nitrato groups after nitration given the less accessibility to the hydroxyl groups of βCXCDs and a higher proportion of cross-linker in the system.

3.5 Compatibility Assessments

Initial compatibility tests based on DSC were carried out to determine whether contact between the βNCPCDs and energetic ingredients in a formulation could lead to undesirable or unexpected hazards. Sample βNCPCD1 was mixed with energetic fillers such as oxidisers, pyrotechnics and high explosives, and preliminary DSC compatibility tests were carried out according to STANAG 4147 Test 4 [25]. Any chemical interaction between the ingredients should lead to a change in the decomposition profile of the formulation. The thermal decomposition of the single ingredients and their mixture was compared (Table 5). The compounds were mixed in a 1:1 w/w ratio (total amount 1.0 mg) and heated from 30 to 500 °C at a rate of 2 °C min^{-1}.

Sample βNCPCD1 was tested with oxidisers such as ammonium dinitramide (ADN), potassium chlorate ($KClO_3$), ammonium perchlorate (NH_4ClO_4) and ammonium nitrate (NH_4NO_3). No changes in either the decomposition temperature (T_{dec}) or the curve shape were observed for mixture βNCPCD1/$KClO_3$ compared to the thermogram of the pure oxidiser (Table 5). We found that βNCPCD1 is not compatible with NH_4ClO_4 or NH_4NO_3 and that ADN shifted the T_{dec} by −13 °C and changed the shape of the curve. Further vacuum stability tests are needed to confirm compatibility with ADN. Sample βNCPCD1 showed good compatibility with pyrotechnics such as red phosphorous. All thermograms are provided in the Supporting Information.

Sample βNCPCD1 also showed good compatibility with symmetric nitro-esters such as pentaerythritol tetranitrate

Table 5. Summary of compatibility tests using βNCPCD1.

Energetic Name	T_{deg} (°C)	Mixture T_{deg} (°C)	ΔT (°C)	Change in shape
ADN	174	161	−13	Significant
KNO_3[1]	–	–	–	Minor
NH_4ClO_4	300	242	−58	Significant
NH_4NO_3[1]	–	–	–	Significant
$KClO_3$[1]	–	–	–	–
Red Phosphorous	400	404	+4	Minor
PETN	185	187	−2	None
HMX	279	279	0	Minor
RDX	225	210	−15	Minor

[1] No degradation observed.

(Figure 8) suggesting that βNCPCDs could potentially be combined with nitroglycerine in double-based and triple-based propellants [26].

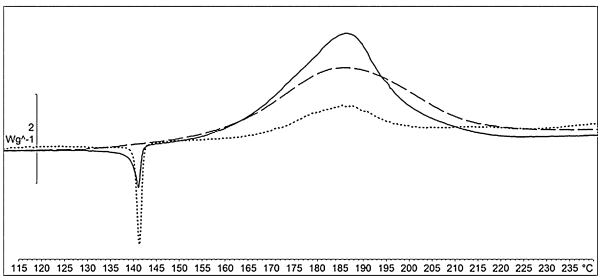

Figure 8. Thermograms of pentaerythritol tetranitrate (dotted line), βNCPCD1 (dashed line) and the mixture (solid line) at 2 °C min^{-1}.

Nitramines such as RDX and HMX were also tested for compatibility with βNCPCD1. Although the T_{deg} of RDX was 15 °C lower when mixed with βNCPCD1, the degradation of HMX was not affected (Figure 9).

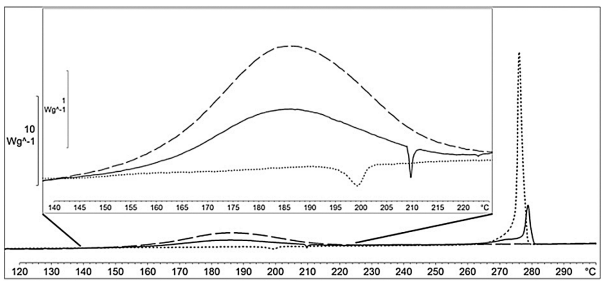

Figure 9. Thermograms of HMX (dotted line), βNCPCD1 (dashed line) and the mixture (solid line) at 2 °C min^{-1}.

The small amount of HMX used in the test underwent degassing within the degradation temperature range of βNCPCD1. The phenomenon was detected by DSC as an endothermic peak at 210 °C. The measurement was repeated several times and the endothermic peak shifted at different temperatures every time, supporting the degassing hypothesis.

4 Conclusions

The synthesis of βCXCD systems from βCD and diglycidyl ethers yielded cross-linked insoluble or water-soluble derivatives with low T_g values down to −30 °C, the first such observation for this type of product. The physicochemical properties of the products were affected by several reaction parameters, including the temperature, cross-linker:βCD ratio, concentration of NaOH, time allowed for the formation of βCD alkoxide, and the duration of reaction with the cross-linker. The cross-linking reaction parameters were tuned to obtain soft, soluble precursors to make the subsequent nitration reaction safer and more consistent. The polymers were water soluble if prepared with a PEGDGE:βCD ratio of up to 5:1 at 30 °C. The T_g of the cross-linked materials was primarily affected by the quantity and length of PEG spacer present in the system.

The βNCPCDs retained some of the mechanical properties of the precursor systems. The T_g was maintained below 0 °C after the nitration of βCPCD derivatives made of high βCD:cross-linker ratio. The presence of polar nitrato groups on the cross-linked molecules increased the packing density of the molecules and thus reduced their freedom, increasing the T_g. Thermal analysis revealed that the nitrated products soften from −60 °C in a linear manner. The thermal stability and energy released by the βNCPCDs is similar to that observed for nitrocellulose samples with a nitrogen content of 12.5–13.5% making them promising nitrocellulose substitutes in energetic compositions. The further processing of βNCXCDs using the same purification methods applied to nitrocellulose would improve the thermal stability even more.

Initial compatibility tests indicated that βNCPCDs may be suitable binders in formulation with selected energetics. The reaction will need to be scaled up for proper compatibility and Energetic Materials Testing and Assessment Policy (EMTAP) tests to determine the sensitivity of the new nitrated cross-linked compounds to ESD.

5 Recommendations/Future work

The assessment of the properties of the new nitrated cross-linked β-cyclodextrins developed in this work is in progress. Investigation of the change of properties with time and overall ageing of the nitrated binder as well as their compatibility with stabilisers/plasticisers is recommended. The cross-linking reaction of βCD with TEGDGE and other ethylene glycol diglycidyl ethers is currently investigated.

Supporting Information

The following files are available free of charge.

Acknowledgements

This project was funded through the Weapons Science and Technology Centre (WSTC) by the Defence Science and Technology Laboratory (Dstl). The authors would like to thank Roxel UK for kindly providing the ADN sample and BAES Land for assistance in the exploitation of this work.

References

[1] H. G. Ang, S. Pisharath, Energetic Polymers, Wiley-VCH., **2012**.
[2] J. Szejtli, Introduction and General Overview of Cyclodextrin Chemistry, *Chem. Rev.* **1998**, 98, 1743–1753.
[3] H. J. Schneider, F. Hacket, V. Rüdiger, NMR Studies of Cyclodextrins and Cyclodextrin Complexes, *Chem. Rev.* **1998**, *98*,1755-1786.
[4] S. Cahill, S. Bulusu, Molecular Complexes of Explosives with Cyclodextrins, *Magn. Reson. Chem.* **1993**, *31*, 731–735.
[5] P. Maksimowski, T. Rumianowski, Properties of the Gamma-Cyclodextrin/CL-20 System, *Cent. Eur. J. Energ. Mater.* **2016**, *13*, 217–229.
[6] J. P. Consaga, Composites of Cyclodextrin Nitrate Ester Plasticizers, United States Patent, 5,114,506, United States Dept. of the Navy, USA **1992**.
[7] J. P. Consaga, Chemically Reactive Fragmentation Warhead, United States Patent, 6,293,201 B1, United States of America, Secretary of the Navy, USA **2001**.
[8] A. Ruebner, G. L. Statton, J. P. Consaga, Polymeric Cyclodextrin Nitrate Esters, United States Patent, 6,527,887, Mach I, Inc., USA **1991**.
[9] G. Mocanu, D. Vizitiu, A. Carpov, Cyclodextrin Polymers, *J. Bioact. Compat. Polym.* **2001**, *16*, 315–342.
[10] C. Rodriguez-Tenreiro, C. Alvarez-Lorenzo, A. Rodriguez-Perez, A. Concheiro, J. J. Torres-Labandeira, New Cyclodextrin Hydrogels Cross-linked with Diglycidylethers with a High Drug Loading and Controlled Release Ability, *Pharm. Res.* **2006**, *23*, 121–130.
[11] T. T. Nielsen, V. Wintgens, K. L. Larsen, C. Amiel, Synthesis and characterization of poly(ethylene glycol) based β-cyclodextrin polymers, *J. Inclusion Phenom. Macrocyclic Chem.* **2009**, *65*, 341–348.
[12] P. Golding, A. J. Bellamy, A. E. Contini, E. Dossi, Polyphosphazenes, Patent WO, WO/2013/190260 A3, Int. Appl. PCT/GB2013/000276, The Secretary of State for Defence, UK; Cranfield University **2013**.
[13] Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, 2006.
[14] E. Dossi, J. Akhavan, S. E. Gaulter, R. G. Williams, W. J. Doe, Cross-linking of Hydroxyl-terminated Polyols with Triethyleneglycol Diglycidyl Ether: An Alternative to Toxic Isocyanates, *Propellants Explos. Pyrotech.* **2018**, *43*, 241–250.
[15] L. B. Romanova, L. S. Barinova, G. V. Lagodzinskaya, A. I. Kazakov, Y. M. Mikhailov, Preparation and NMR Analysis of β-Cyclodextrin Nitrates, *Russ. J. Appl. Chem.* **2014**, *87*, 1884–1889.
[16] W. J. Doe, New PBX formulations free of toxic isocyanates, MSc Thesis, Cranfield University, Shrivenham, UK, **2012**.
[17] G. Tripodo, C. Wischke, A. Lendlein, Highly Flexible Poly(ethyl-2-cyanoacrylate) Based Materials Obtained by Incorporation of Oligo(ethylene glycol)diglycidylether, *Macromol. Symp.* **2011**, *309/310*, 49–58.
[18] R. Khan, P. Forgo, K. J. Stine, V. T. D'Souza, Methods for Selective Modifications of Cyclodextrins, *Chem. Rev.* **1998**, *98*, 1977–1996.
[19] E. Gaidamuskas, B. Norkus, E. Botkus, D. C. Crans, G. Grinciene, Deprotonation of β-cyclodextrin in alkaline solutions, *Carbohyd. Res.* **2009**, *344*, 250–254.
[20] P. Mischnick, D. Momcilovic, Chemical Structure Analysis of Starch and Cellulose Derivatives, *Adv. Carbohydr. Chem. Biochem.* **2010**, *64*, 117–210.
[21] G. Norwitz, Spectrophotometric Determination of sulfate in propellants and nitrocellulose, Department of the Army Frankford Arsenal, AMS code 4931.OM.6350, Philadelphia, 1970, http://www.dtic.mil/dtic/tr/fulltext/u2/711884.pdf (cited October **2017**).
[22] A. G. Bricknell, L. W. Trevoy, J. W. T. Spinks, A study of the sulfate in nitrocellulose using S35O4 – as tracer, *Can. J. Chem.* **1957**, *35*, 704–14.
[23] Porter, D. Group Interaction Modelling of Polymer Properties; Marcel Dekker: New York, **1995**.
[24] S. M. Pourmortazavi, S. G. Hosseini, M. Rahimi-Nasrabadi, S. S. Hajimirsadeghi, H. Momenian, Effect of nitrate content on thermal decomposition of nitrocellulose, *J. Hazard. Mater.* **2009**, *162*, 1141–1144.
[25] NATO Standardization Agreement STANAG 4147, Chemical Compatibility of Ammunition Components with Explosives and Propellants (Non-Nuclear Application), **1992**.
[26] J. Akhavan, The Chemistry of Explosives, The Royal Society of Chemistry, Cambridge, **1998**.

Received: May 1, 2018
Revised: July 18, 2018
Published online: ■■, ■■■

FULL PAPER