

2,4-Dinitrophenyl Ether of Polyvinyl Alcohol and Polymer Bound Anionic SIGMA Complexes

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Abstract

A new electrophilic polymer, 2,4-dinitrophenyl ether of polyvinyl alcohol (PVA-DNP), having a degree of substitution of 0.5 was prepared from polyvinyl alcohol (PVA) and 1-fluoro-2,4-dinitrobenzene (DNFB). The PVA-DNP polymer was characterized by NMR, IR, and UV-visible spectroscopy. The reaction of PVA-DNP with sodium methoxide was followed by NMR and UV-visible spectroscopy. Evidence of polymer bound spirocyclic SIGMA complex, C-1 and C-3 polymer bound DNP-methoxy SIGMA complexes and the formation and C-1 methoxy complex of 2,4-dinitroanisole was observed.

Keywords

2,4-Dinitrophenyl Ether, Polyvinyl Alcohol, Anionic SIGMA Complex, Thermal Stability, Nucleophilic Aromatic Substitution

1. Introduction

Nitro-substituted aromatic compounds, also known as electron deficient aromatics, are of interest in organic synthesis and as high-energy materials [1]-[6]. When used in organic synthesis, these compounds can be transformed into new substances through nucleophilic aromatic substitution (S_NAr). In S_NAr reactions, anionic SIGMA complexes are formed as intermediates as shown in **Scheme 1**. When electron deficient aromatics contain two or more electron withdrawing groups and X is a poor leaving group, stable isolable anionic SIGMA complexes are formed. These anionic SIGMA complexes are deep red in color and explosive. In addition to being useful intermediates in organic synthesis, electron deficient aromatics containing two or more nitro groups find use in explosives and solid propellants [5] [6] [7] [8] [9]. Although trinitro aromatic compounds are more energetic than dinitro aromatic compounds, these compounds have some

disadvantages. Drawbacks to trinitro aromatic compounds such as trinitrotoluene (TNT) include high vapor pressure, toxicity, and environmental concerns [6]. As a result, the development of insensitive munitions (IM) with reduced toxicity and lower vapor pressure has become a key part of modern explosives research [6]. In recent years, 2,4,6-trinitrotoluene (TNT) has fallen out of favor as an ingredient in melt-cast explosive formulations, while 2,4-dinitrophenyl ethers have emerged as alternatives with desirable chemical and physical properties [5] [6]. Interest in insensitive melt cast explosive formulations and anionic SIGMA complexes prompted us to prepare PVA-DNP and explore its chemical and thermal properties. The influence of a polymeric backbone and neighboring functionality on anionic SIGMA complex formation and stability is of particular interest. The chemistry of nitroaromatics in a PVA matrix is also of interest since a test kit for detecting nitroaromatic explosives employing a PVA-glycerin gel infused with base has recently been reported [10]. With this test kit, a sample containing nitroaromatic explosive material is mixed with the PVA gel containing base. If nitroaromatic explosives are present, highly colored anionic SIGMA complexes are formed [10]. Based on this report, it is unclear whether PVA participates in anionic SIGMA complex formation. Our investigation of the reaction of PVA-DNP with a strong base (NaOCH_3) provides insights regarding how nitroaromatic explosive materials interact with a PVA matrix under basic conditions. The PVA-DNP polymer described in this work is ideal for investigating $\text{S}_{\text{N}}\text{Ar}$ and SIGMA complex forming reactions of explosive nitroaromatic compounds in a PVA matrix.

2. General Methods and Procedures

Polyvinyl alcohol (100% hydrolyzed, MW 14,000), 1-fluor-2,4-dinitrobenzene, triethylamine, toluene and diethyl ether were used as received. N,N,- dimethylformamide (DMF) and deuterated dimethyl sulfoxide (DMSO-d₆), were stored over molecular sieves prior to use. Methanol was refluxed over magnesium turnings and distilled before use. Sodium methoxide was prepared from freshly distilled methanol and sodium metal. The PVA-DNP polymer was prepared and purified as follows: To a stirred solution of PVA (0.53 grams) dissolved in DMF (25 mL) was added triethylamine (3.5 mL), and 1-fluor-2,4-dinitrobenzene (2.30 grams). The solution was heated at 70 °C for 7 days followed by removal of DMF by rotary evaporation to yield a dark red oily substance. The red oil was poured into a 10% solution of HCl (100 mL) to yield a rubbery solid. The solid was washed successively with cold water (14 × 50 mL), diethyl ether (14 × 50 mL) and then dried. The dried solid was further purified by Soxhlet extraction first with toluene (24 hours), then with diethyl ether (24 hours) and finally with methanol (25 hours). After drying, 0.90 grams PVA-DNP polymer (tan powder) having a degree of substitution of 0.5 was obtained. IR (KBr) 3530, 3400, 3080, 2930, 1610, 1510, 1530, 1480, 1345, 1270, 1150, 1060, 920, 900, 825, 735, 705, 635 cm^{-1} . UV max (methanol) 300 nm. An NMR spectrum of PVA-DNP is pro-

vided in **Figure 1**.

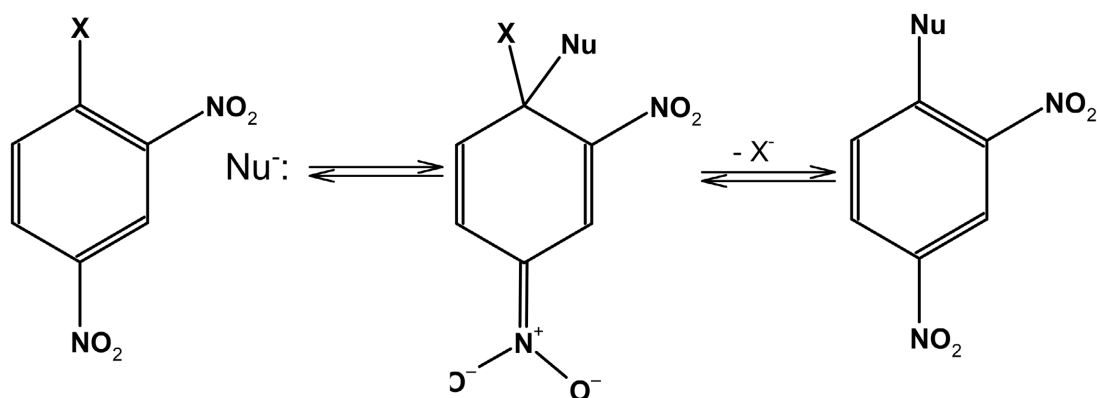
Methods

In order to obtain NMR spectra, all compounds were dissolved in DMSO-d₆. NMR spectra were obtained with a Bruker 270 mega-hertz spectrometer. All chemical shifts are reported in part per million (ppm) with respect to internal tetramethyl silane. Infrared spectra were recorded using a Perkin Elmer 1430 spectrometer. UV-visible spectra were recorded using a Perkin Elmer Lambda 4B spectrometer.

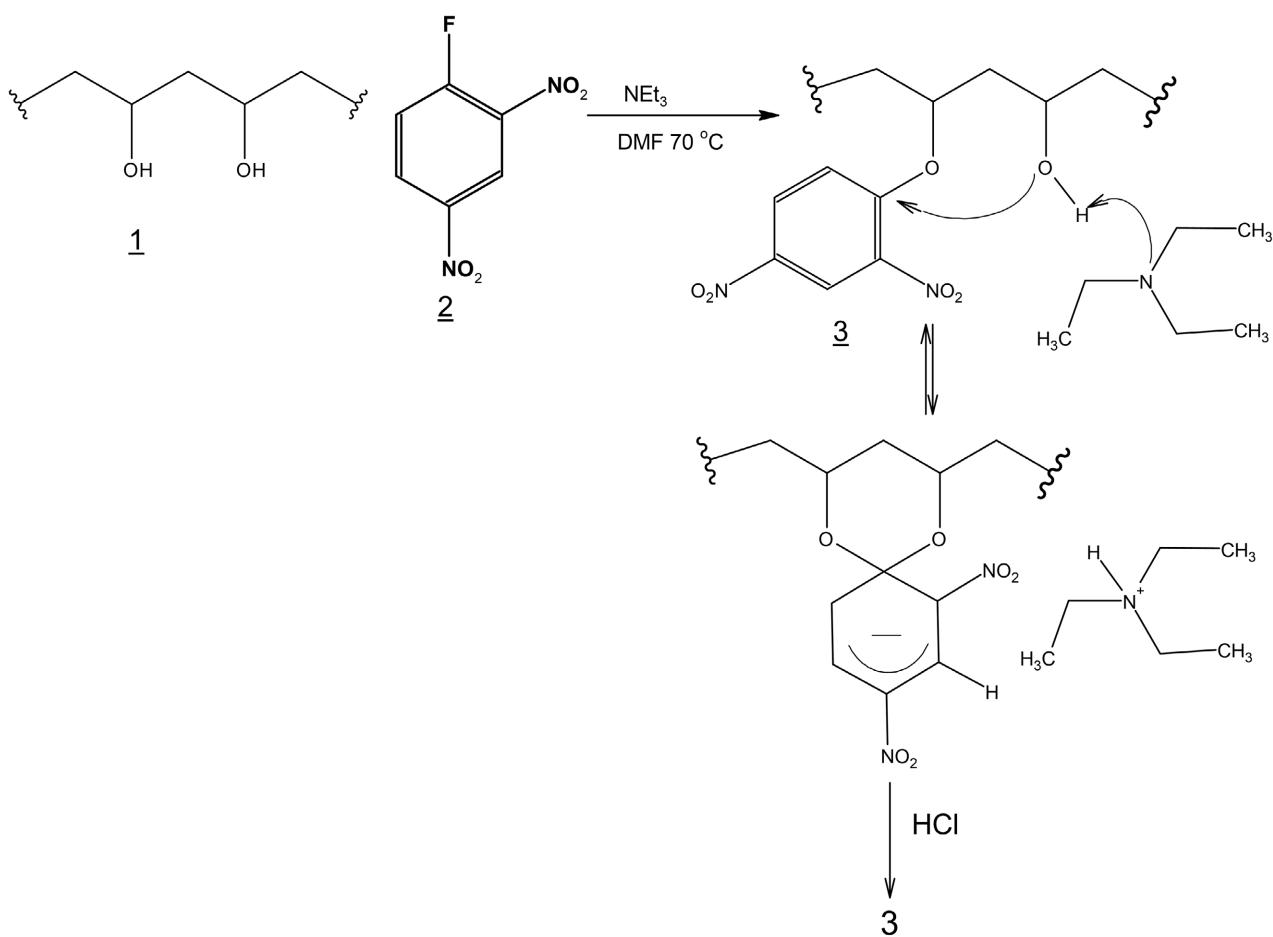
3. Results

3.1. Synthesis and Characterization of PVA-DNP

PVA-DNP was synthesized through a triethylamine catalyzed reaction of 1-fluoro-2,4-dinitrobenzene (DNFB) with polyvinyl alcohol in dimethylformamide (DMF) as shown in **Scheme 2**. One equivalent of DNFB per equivalent of PVA hydroxyl group was used and the reaction was conducted at 70 °C for 7 days to yield PVA-DNP with a degree of substitution (DS) of 0.5. The reaction mixture remains deep red even after heating at 70 °C for 7 days and the color does not fade until the reaction is neutralized with HCl. Our results are consistent with the initial formation of a PVA-DNP ether which is followed by an intramolecular reaction leading to a spirocyclic anionic SIGMA complex. This red color is indicative of anionic SIGMA complex formation. The known ease of intramolecular reaction to form spirocyclic anionic SIGMA complexes and the propensity of PVA to form acetals and ketals accounts for the degree of substitution being limited to 0.5 as shown in **Scheme 2** [11] [12] [13] [14] [15]. Upon neutralization, the deep red color of the reaction mixture fades indicating decomposition of the spirocyclic anionic SIGMA complex. The PVA-DNP polymer is stable up to about 277 °C at which point 2,4-dinitrophenol is released rather than exploding. The 2,4-dinitrophenol was identified by melting point, infrared spectroscopy and mass spectroscopy. A more detailed study of the thermal behavior of PVA-DNP and model compounds will be reported separately.



Scheme 1. Example of nucleophilic aromatic substitution (S_NAr) in which X is a leaving group (F, Cl, Br), and Nu⁻ is a nucleophile.



Scheme 2. Synthesis of PVA-DNP having 0.5 degree of substitution.

3.2. NMR Characterization of PVA-DNP

The NMR spectrum of PVA-DNP shows three broad peaks in the region between 9.0 and 6.8 ppm which are consistent with polymer bound 2,4-dinitrophenyl ether units. The DNP peaks in PVA-DNP are broadened due to the slow tumbling of polymer chains and torsional strain. Based on the model compound, 2,4-dinitroanisole, these peaks correspond to C3 (H_d), C5 (H_f) and C6 (H_g) protons of polymer bound 2,4-dinitrophenyl ether. The DNP protons from PVA-DNP are shifted up field compared to those of 2,4-dinitroanisole. This is likely from the hydrogen bonding of PVA hydroxyl groups with DNP nitro-groups. In addition, the methine and methylene peaks in PVA-DNP are shifted down field compared to those in unsubstituted PVA (**Figure 1**).

3.3. Infrared Analysis PVA-DNP

Infrared spectra of PVA-DNP and PVA both display broad absorption bands near 3400 cm^{-1} characteristic of hydrogen bonded hydroxyl groups. However, the OH band in PVA-DNP also shows a sharp peak near 3550 cm^{-1} indicating the presence of some non-hydrogen bonded OH groups. In addition, the ratio of OH to C-H aliphatic bands is significantly less in the PVA-DNP compared to

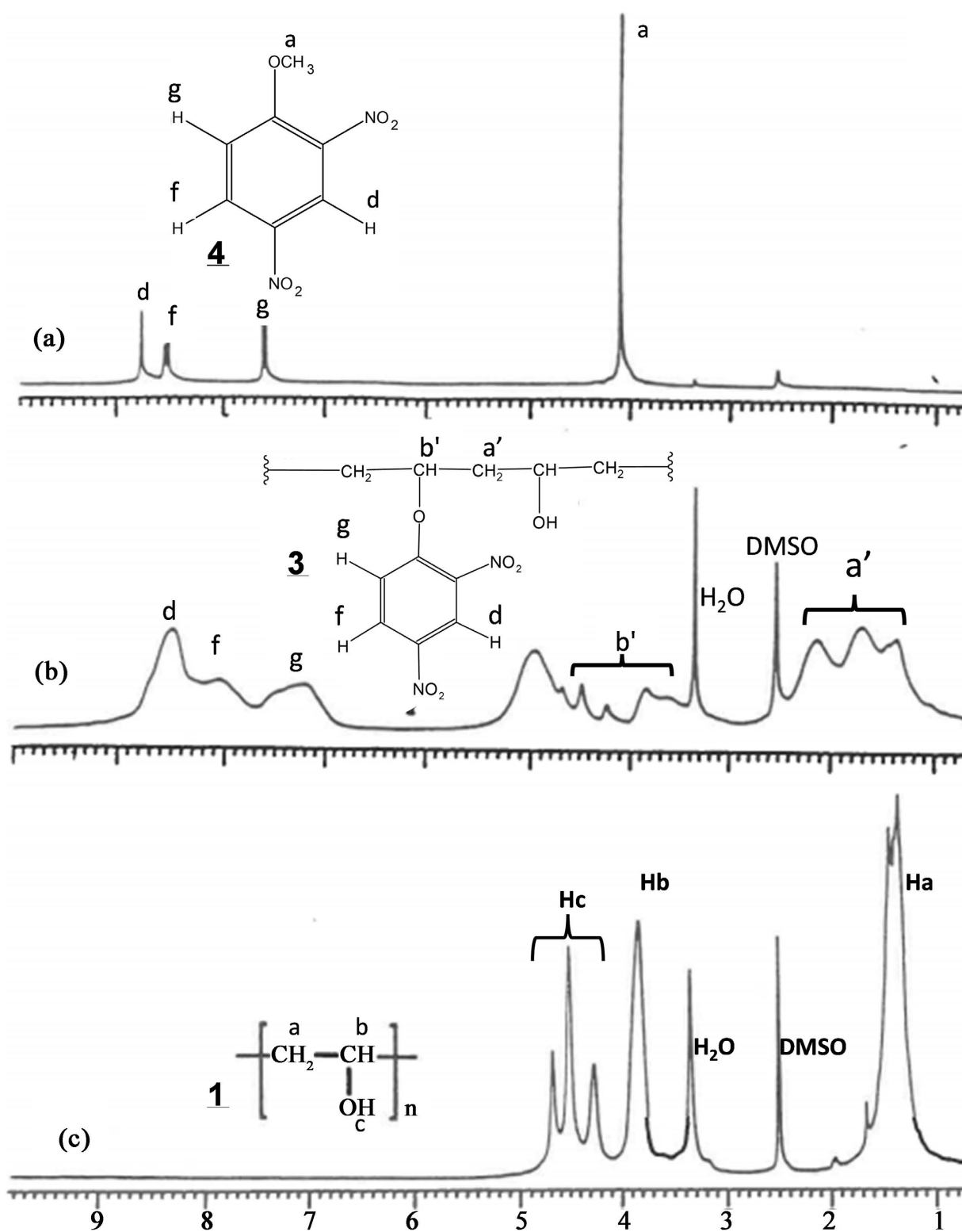


Figure 1. 270 MHz NMR spectra of (a) 2,4-dinitroanisole, (b) PVA-DNP, and (c) PVA.

PVA. The infrared spectrum of PVA-DNP shows C-H aromatic bands near 3100 cm^{-1} characteristic of dinitrophenyl rings. Additional bands characteristic of dinitrophenyl ether structure are found at 1610 cm^{-1} (C=C aromatic), 1530 cm^{-1}

(NO₂ asymmetric stretch), and 1345 cm⁻¹ (NO₂ symmetric stretch).

3.4. PVA-DNP Anionic SIGMA Complexes

The interaction of PVA-DNP with sodium methoxide was investigated by NMR spectroscopy. Upon addition of two equivalents of sodium methoxide to a DMSO-d₆ solution containing PVA-DNP, the solution turns deep red and several new peaks in the NMR spectrum are observed in the region between 5.5 ppm and 9.0 ppm. Three of the peaks in this region correspond to the 1,1-methoxide SIGMA complex of 2,4-dinitroanisole. The presence of 1,1-methoxide complex of 2,4-dinitroanisole, **5**, was confirmed by independently preparing it from 2,4-dinitroanisole and sodium methoxide. The NMR spectrum (**Figure 2**) of the reaction of PVA-DNP with sodium methoxide also shows multiple new signals in the region between about 8.3 ppm and 8.8 ppm corresponding to C-3 DNP protons from different SIGMA complexes (Structures 4, 5, and 6). In addition,

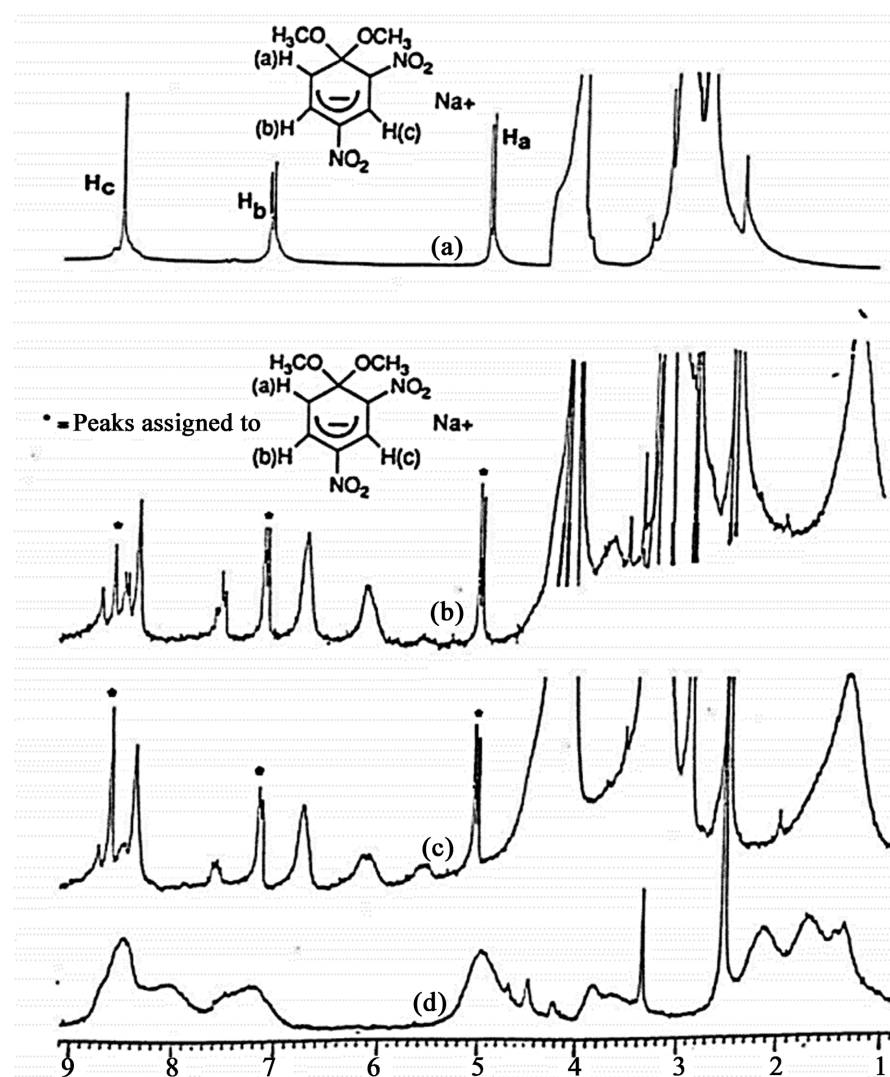


Figure 2. NMR spectrum (270 MHz) of PVA-DNP plus two equivalents of sodium methoxide in methanol.

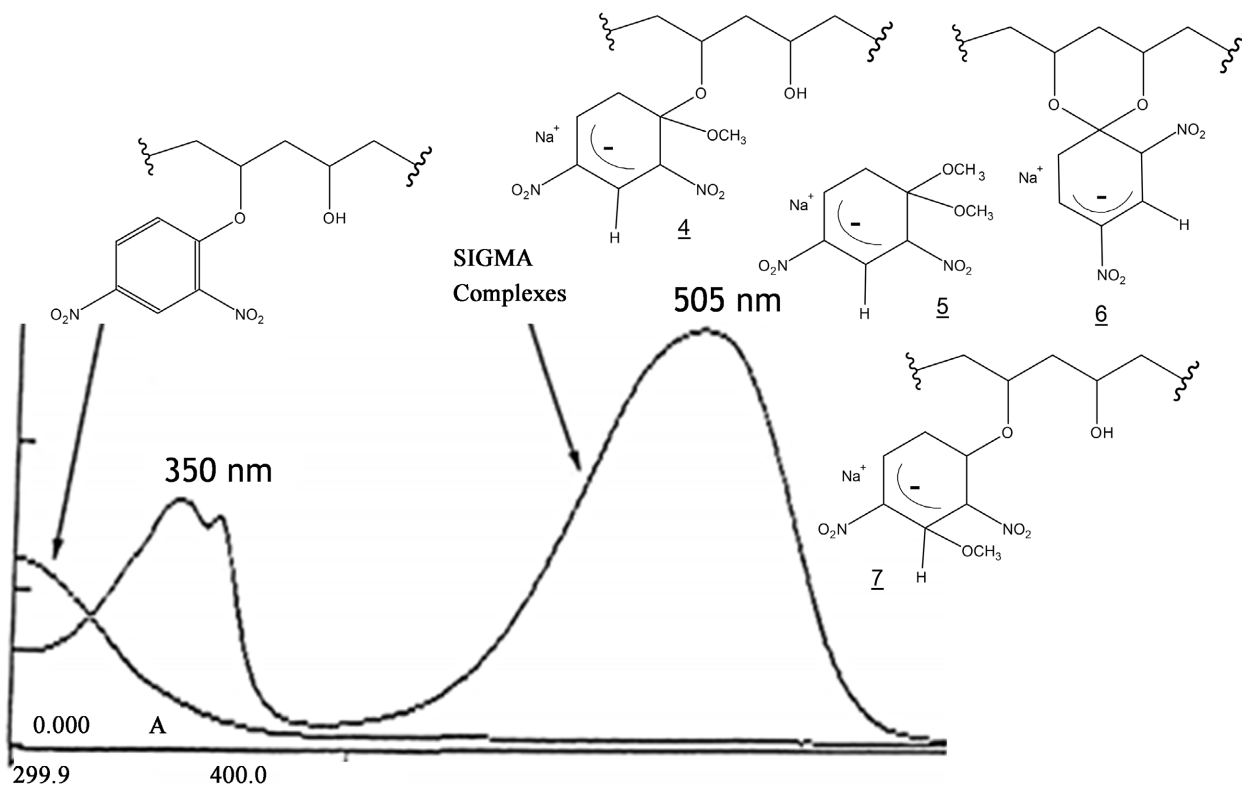
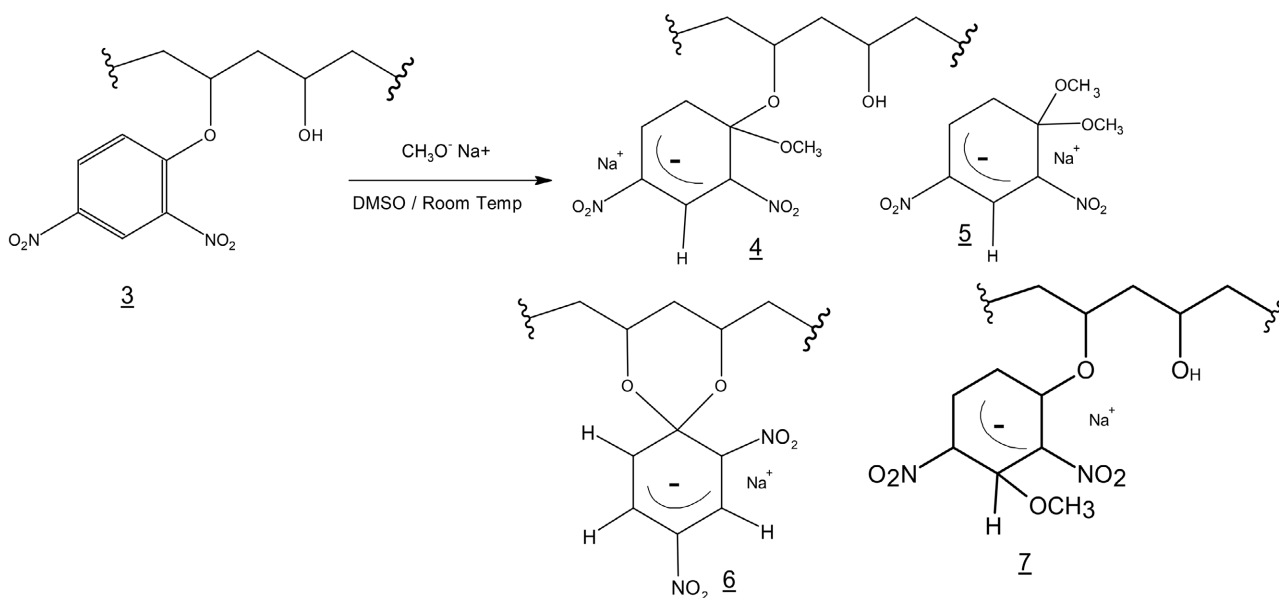


Figure 3. UV-visible spectrum of PVA-DNP polymer plus two equivalents of sodium methoxide in methanol.



Scheme 3. Reaction of PVA-DNP polymer with two equivalents of sodium methoxide.

the NMR spectrum shows transient peaks near 5.5 ppm which are characteristic of sp^3 hybridized ring hydrogens in 1,3 adducts such as **Z**. The formation of five and six membered spirocyclic SIGMA complexes are known to form readily [11] [12]. Anionic SIGMA complex formation of PVA-DNP with sodium methoxide was also investigated by UV-visible spectroscopy. The addition of two equiva-

lents of sodium methoxide to a methanol solution of PVA-DNP resulted in the immediate formation of a deep red solution which had maxima near 350 nm and 505 nm, as shown in **Figure 3**. These absorptions are characteristic of anionic SIGMA complexes like those shown in **Scheme 3**.

3.5. Conclusion

Interest in melt cast insensitive munitions prompted us to prepare PVA-DNP and investigate anionic SIGMA complexes made from it. The PVA-DNP was prepared by S_NAr substitution of DNFB by PVA in DMF. During the synthesis of PVA-DNP, neighboring group effects of PVA hydroxyl groups limited the DS to 0.5. The PVA-DNP polymer was shown to be stable up to about 277°C at which point 2,4-dinitrophenol was eliminated rather than detonated. In addition, the PVA-DNP polymer formed stable anionic SIGMA complexes when treated with sodium methoxide. The PVA-DNP polymer of this work and its anionic SIGMA complexes are of potential use in IM formulations and solid propellants.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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