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On Calculating Polymeric Binders' Enthalpy of Formations and Band Gaps with Computational Methods

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Abstract: Enthalpy of formations and band gaps of polymeric binders are important parameters while designing explosive/propallent compositions. We have explored the computational methods towards the determination of enthalpy of formations and band gaps of polymeric binders by considering their respective oligomeric forms. Initially, we have computed enthalpy of formation of known non-energetic binder hydroxy terminated polybutadiene (HTPB). The applied computational methodology has been shown that the calculated enthalpy of formation is closely related to the experimentally determined enthalpy of formation of HTPB. The applied computational methodology has also been validated with known energetic binder glycidyl azide polymer GAP by means of calculated enthalpy of formations. Further, enthalpy of formation of azido HTPB (AHTPB) has been calculated in the direction of achieving energetic, insensitive and compatible polymeric binder. In this study, the extrapolation techniques on the oligomers were used to obtain the enthalpy of formation whereas periodic bond condition (PBC) computations on the dimers for band gap values of polymers. Highly positive enthalpies of formation of oligomers of AHTPB compared to that of HTPB and GAP suggests that AHTPB can be a potential energetic binder in explosive compositions. From the periodic bond condition (PBC) - frontier molecular orbital band gap studies, it has been observed that the stability or insensitivity order of these polymeric binders should be HTPB > GAP > AHTPB. Superior curable nature of AHTPB over HTPB has been examined with the help of interaction energies. These results are vital in the quest for molecular-based predictions to polymer properties in general but in particular it is an encouraging result for the study of polymers with monomer of relatively large molecular weight.

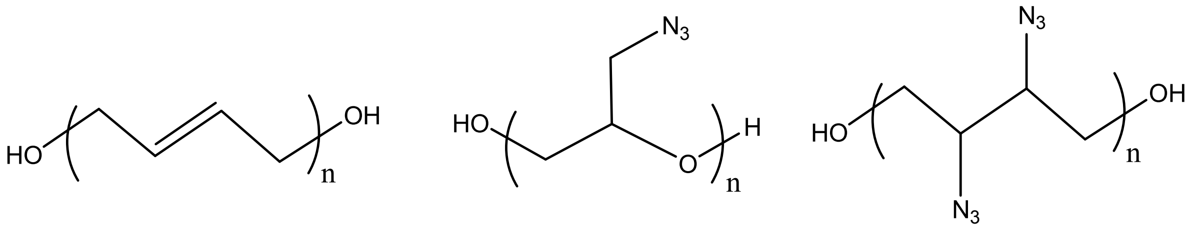
Keywords: Enegetic Binders; Non-Energetic Binders; Enthalpy of Formations; Band Gaps; HTPB.

Introduction

The mixture comprises mainly a low molecular weight prepolymer, solid energetic material/oxidizer and plasticizer was identified as composite propellant in the form of cross-linked polyurethanes.[1] This low molecular weight prepolymer is often called as binder. Binders are compositions that hold together a charge of finely divided solid particles and increase the mechanical strength of the resulting propellant grain. Such binders usually are functionally terminated prepolymers such as hydroxyl-terminated polybutadiene (HTPB), carboxyl-terminated polybutadiene (CTPB) resins, plastics, or asphaltics used dry or in solution. Ideal binder should have more positive enthalpy of formation and must have suitable structure, which on combustion produces low molecular weight gases, thereby leading to high specific impulse (I_{sp}) and also needs to find applications in adhesives and sealants, etc.[2] Out of the different types of new binders synthesized and characterized, the following binders are promising candidates with regard to above factors. They are glycidyl azide polymer (GAP), poly-3,3-bis (azidomethyl) oxetane (BAMO), poly glycidyl nitrate (PGN), poly-3-nitratomethoxy-3-methyl oxetane (PLN) and their copolymers.[3] GAP and poly BAMO are unique highly energetic materials containing endothermic azido groups in the polymer chain. Binders may be classified as inert (e.g. HTPB) and/or energetic (e.g. GAP) on the basis of their energetics i.e capability of undergoing internal oxidation-reduction, gas-forming decomposition and exothermic.[4] The most commonly used fuel binder in composite solid propellants all over the world is HTPB which is liquid prepolymer having excellent physical properties such as low glass transition temperature, high tensile and tear strength, and good chemical resistance.[5] Modified or unmodified highly hydrophobic HTPB based polyurethanes were introduced earlier for selective adsorption of protein, for selective gas transport properties and for separation of ethanol–water mixture.[6-11] The promising scenery of this fuel binder for poly-urethane propellant is due to hydrocarbon nature of HTPB along with low viscosity, insensitive nature and low specific gravity (0.90 g/cm^3). HTPB is proficient of appealing solid loading up to 86-88% without sacrificing the simplicity of processibility.[12] In most solid rocket propellants, the inert binder (HTPB) comprises only 5-15% of the total propellant formulation and affects the final properties of the propellant by reducing the achievable output energy due to its less positive or negative heat of formation in contrast to its excellent favourable mechanical properties as mentioned above. These facts prompted us to make HTPB more energetic via azidation by keeping all its physical properties unaltered. For this purpose, we have attempted to determine the enthalpies of formation of oligomeric HTPB with and without azidation. Further, known energetic binder GAP has been considered in a similar fashion in order to evaluate the relative magnitude of positive enthalpy of formation achieved for AHTPB as a result of azidation.

One property commonly calculated for explosive ingredient molecules is the heat of formation (HOF). It is usually taken as the indicator of the “energy content” of high energy materials. Therefore, it is very important to predict the heat of formation accurately. However, it is impractical to determine the HOFs of new energetic materials because of their unstable intermediates and unknown combustion mechanism. Moreover, due to the limited computer resources existing, it is even impossible to calculate the properties of the polymer. For this purpose, a possible approach consists in the calculation of a series of increasingly large oligomers from where an asymptotic behaviour can be obtained. Information on the evolution of oligomeric properties with chain length is needed to correlate molecular properties with the corresponding properties of polymers. Thus, the properties of shorter chain oligomers from monomer to pentamer units of HTPB, AHTPB and GAP (Scheme 1) were calculated in an attempt to determine how the properties of the chain change with an increasing number of monomer units and how many monomer units are required to estimate the polymer properties.

It has been shown that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) plays a major role in governing the reactivity of organic compounds.[13] The spark sensitivity has been correlated with the HOMO-LUMO gap of energetic material.[14] Generally, smaller is the HOMO-LUMO gap, easier the electron shift and larger the sensitivity and so the poorer the stability of the compound, whereas, higher is the HOMO-LUMO gap, difficult the electron shift and larger the insensitivity and increases the stability under the stimuli of impact and shock due to its electron donating nature.[15,16] It has also been shown that the extrapolation method at B3LYP/6-31G(d) level of theory predicts the band gap of conjugated polymers (polythiophene, polypyrrole, polyfuran, etc.) quite accurately when long conjugated oligomers are used.[17] Since, the studied polymers in the present work are non-conjugated, band gaps have been determined at PBC/B3LYP/6-31G(d) in order to obtain relative sensitivity or insensitivity of HTPB, AHTPB and GAP polymeric binders.



HTPB GAP AHTPB

Scheme 1 Polymeric binders considered for oligomeric study.

Results and Discussion

This study employed linear fit extrapolation method for calculating enthalpy of formation and band gaps of polymeric binders at MP2/6-31+G(d)//B3LYP/6-31G(d) level of theory. The process consists of three major steps. In the first step, geometry optimization calculations were carried out on oligomers of HTPB, GAP and AHTPB (Figures 1−3). In second step, the enthalpies of formations of oligomers were determined using corresponding atomization reactions. In the third step, band gaps of oligomers were calculated by taking into account the energy difference of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels.

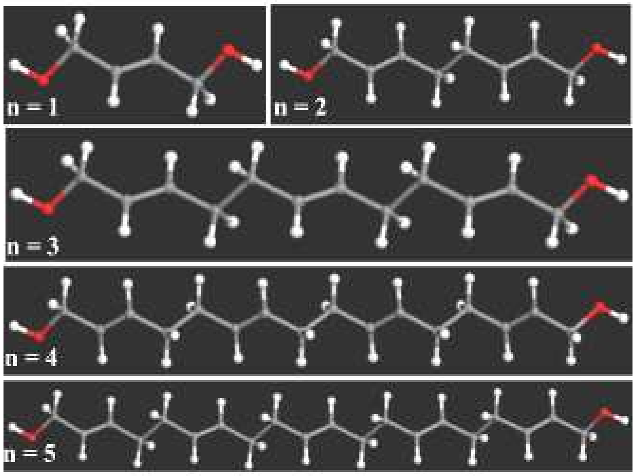


Fig. 1 B3LYP/6-31G(d) optimized geometries of monomer and oligomers of HTPB with n = 2 to 5 (grey = carbon, red = oxygen and white = hydrogen).

Enthalpy of formations (ΔH_f):

The computed enthalpies of formations of HTPB, GAP and AHTPB oligomers (monomer to pentamer) are presented in Table 1. The enthalpies of formation of monomer, dimer, trimer, tetramer and pentamers of HTPB were found to be -184.6 kJ/mol, -95.1 kJ/mol, -5.1 kJ/mol, 84.4 kJ/mol and 174.8 kJ/mol, respectively Table 1. These values are exactly an incremental by a value 90 kJ/mol from left to right. Therefore, we found an exact linear correlation ($R^2 = 1$) between enthalpies of formation (ΔH_f) and number of monomer units (n) of HTPB (Figure 4a). We have extended this linearity to higher degree of oligomers in order to predict their enthalpy of formation by extrapolation method. The HTPB polymer encompassing a molecular weight of the range 2000 – 3000 is commonly used in explosive formulations.[2,5] Therefore, the enthalpies of formation of HTPB polymer for the 2000 – 3000 range of molecular weights were obtained by this extrapolation method. They are found to be in the range 3000 – 4700 kJ/mol. But there is no experimental enthalpy of formation value available in the literature in this range of molecular weights. However, the experimental enthalpy of formation of HTPB with a molecular formula $[C_{10}H_{15.4}O_{0.07}]_n$ where n = 1, has been reported which is equal to −51.9 kJ/mol.[18,19] The molecular weight calculated from this molecular formula is 136.5 and the corresponding enthalpy of formation obtained from linear fit extrapolation method was found to be −105.2 kJ/mol. This theoretical enthalpy of formation value differs from experimental value by 53.3 kJ/mol only. Therefore, the computational methods and modeling approaches employed in this study are reasonably in agreement with the available experimental results.

Table 1 Calculated total energy (E_0, au) and enthalpies of formations, (ΔH_f, kJ/mol) at MP2/6-31+G(d)//B3LYP/6-31G(d), along with Zero Point Vibrational Energy (ZPVE, au), and Thermal Correction (H_T, au) at the B3LYP/6-31G(d) Level for oligomers of HTPB, GAP and AHTPB (n =1 to 5).

SNo	*Oligomer*	E_0	*ZPVE*	H_T	ΔH_f
1	HTPB-1	-306.69375	0.11824	0.12675	-184.59958
2	HTPB-2	-462.16637	0.20879	0.22226	-95.09018
3	HTPB-3	-617.63890	0.29918	0.31771	-5.08556
4	HTPB-4	-773.11153	0.38981	0.41329	84.34934
5	HTPB-5	-928.58392	0.48018	0.50877	174.84131
6	GAP-1	-431.92288	0.11722	0.12717	69.64180
7	GAP-2	-787.63963	0.21066	0.22844	319.13360
8	GAP-3	-1143.35942	0.30438	0.32994	560.53610
9	GAP-4	-1499.07956	0.39818	0.43147	800.87499
10	GAP-5	-1854.79983	0.49190	0.53295	1040.93452
11	AHTPB-1	-634.28239	0.14885	0.16282	439.77637
12	AHTPB-2	-1117.34021	0.26956	0.29429	1163.57924
13	AHTPB-3	-1600.39962	0.39022	0.42574	1883.27950
14	AHTPB-4	-2083.45920	0.51097	0.55725	2602.46984
15	AHTPB-5	-2566.51885	0.63169	0.68875	3321.51041

Wide ranges of experimental enthalpy of formation values, 95 − 490 kJ/mol were reported[20-22] for energetic binder GAP, however, their respective molecular weights are not available in the literature to correlate. The optimized geometries of monomer and oligomers (dimer to pentamer) of GAP are depicted in Figure 2. From the calculated enthalpies of formation values of monomer and oligomers (dimer to pentamer) of GAP as shown in Table 1, it was found that the incremental value is ~240 kJ/mol. The linear correlation obtained between enthalpies of formation ($\Delta \boldsymbol{H_f}$) and number of monomer units (**n**) of GAP has shown a best fit with $R^2 = 0.999$ (Figure 4b). The molecular weight of GAP samples used in experimental studies for the preparation of highly energetic solid rocket propellant has ranged from 700 to 5500. The extended linearity to higher degree of oligomers predicted their enthalpy of formation by extrapolation method for this range of molecular weights to be in the range 935 – 12935 kJ/mol. But the experimental enthalpy of formation value of GAP available in the literature is 117.2 kJ/mol for molecular formula $[C_3H_5N_3O]_n$ where n = 1.[18] For molecular weight obtained from this molecular formula, the enthalpy of formation obtained through linear fit extrapolation method was found to be 30.8 kJ/mol. Again the variation caused in this case between experimental and theoretical enthalpy of formation values was found to be 86.4 kJ/mol only.

Although the theoretical values are nearly 50-80 kJ/mol smaller than the experimental values in these cases, it is evident from the above enthalpies of formation values that the experimental trend is correctly predicted by the theoretical calculations despite the fact that the complicated nature under which electrons move along the polymeric chain was simplified to a simple monomers or oligomers (dimer to pentamer), the effects of disorder and three dimensional interactions of polymer chains were totally ignored. Therefore, the method employed in this study can be considered for the further prediction of enthalpy of formation of AHTPB, a newly proposed energetic polymeric binder. As there is no experimental or theoretical enthalpy of formation data available for AHTPB polymer, we have compared its enthalpy of formation with HTPB and GAP polymeric binders. The incremental value for enthalpy of formation from monomer to pentamer of AHTPB is ~ 720 kJ/mol. Plotting (Figure 4c) of number of monomer units against corresponding enthalpies of formation leads a linear correlation (R^2 = 1) as observed in HTPB and GAP cases. According to these calculations, the relative enthalpy of formation order of oligomers is AHTPB > GAP > HTPB. (Table 1) The overall study reveals that, compared to the enthalpies of formations of HTPB and GAP, the presence of nitrogen-rich azido groups in proposed polymer (AHTPB) dramatically increases the enthalpy of formation (Table 1 & 2).

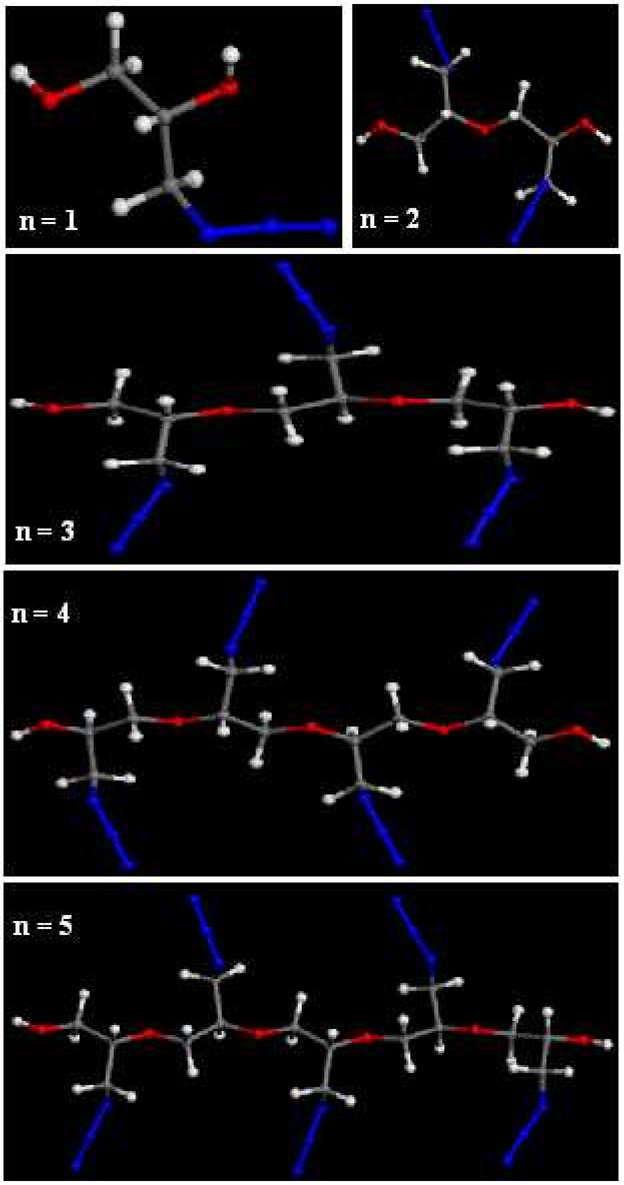


Fig. 2 B3LYP/6-31G(d) optimized geometries of monomer and oligomers of GAP with n = 2 to 5 (grey = carbon, red = oxygen, blue = nitrogen and white = hydrogen).

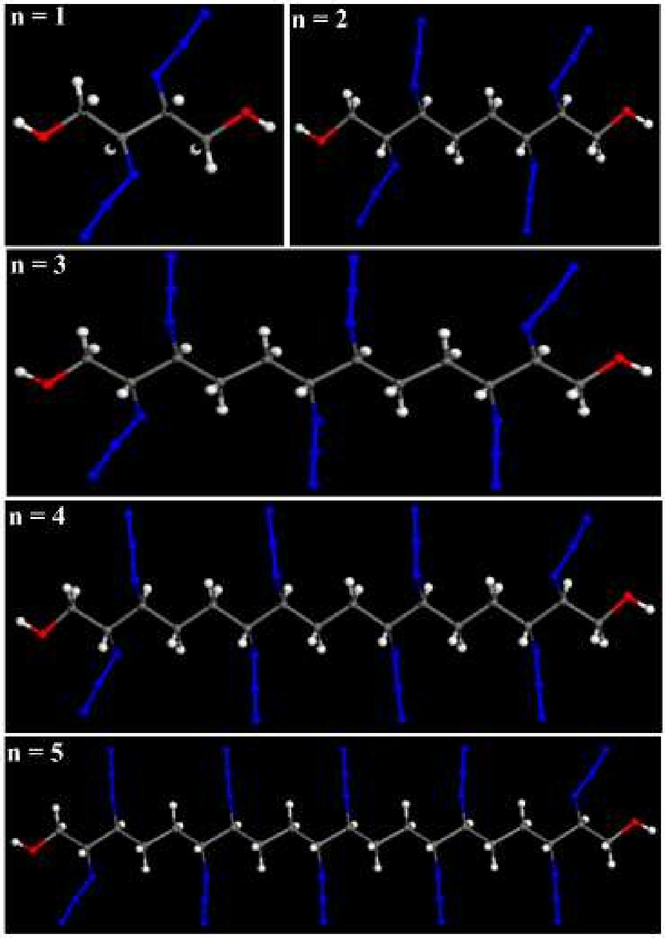


Fig. 3 B3LYP/6-31G(d) optimized geometries of monomer and oligomers of AHTPB with n = 2 to 5 (grey = carbon, red = oxygen, blue = nitrogen and white = hydrogen).

It is important to know the relative magnitudes of changes in the enthalpies of formation of given low molecular weight polymers. Therefore, we have predicted the enthalpy of formations of HTPB, GAP and AHTPB by keeping the number of repeating unit constant as shown in scheme 1, say for example **n** = 20 using the above linear fit extrapolation method. The molecular weights for HTPB, GAP and AHTPB with n = 20 are 1114, 1998 and 2754, for which the corresponding computed enthalpies of formations were found to be 1540 kJ/mol, 4825 kJ/mol and 19614 kJ/mol, respectively. The proposed AHTPB with n = 20 shown that the increment in the enthalpy of formation value by ~18000 kJ/mol compared to inert binder HTPB. Similarly, AHTPB (n = 20) shown the positive enthalpy of formation by a factor of ~ 15000 kJ/mol compared to energetic binder GAP (n = 20). Therefore, the proposed AHTPB can work as a suitable energetic polymeric binder in explosive compositions in place of HTPB.

Table 2 Enthalpies of formations (ΔH_f) (kJ/mol) for polymeric binders along with their corresponding molecular weights.

Entry	HTPB	GAP	AHTPB
Experimental ΔH_f (M_W)	-51.9 (136.5)	117.2 (99.2)	–
Calculated ΔH_f (M_W)	3086 –4722 (2032 – 3004)	1576 – 13575 (711 – 5463)	14614 – 21614 (2074 – 3026)

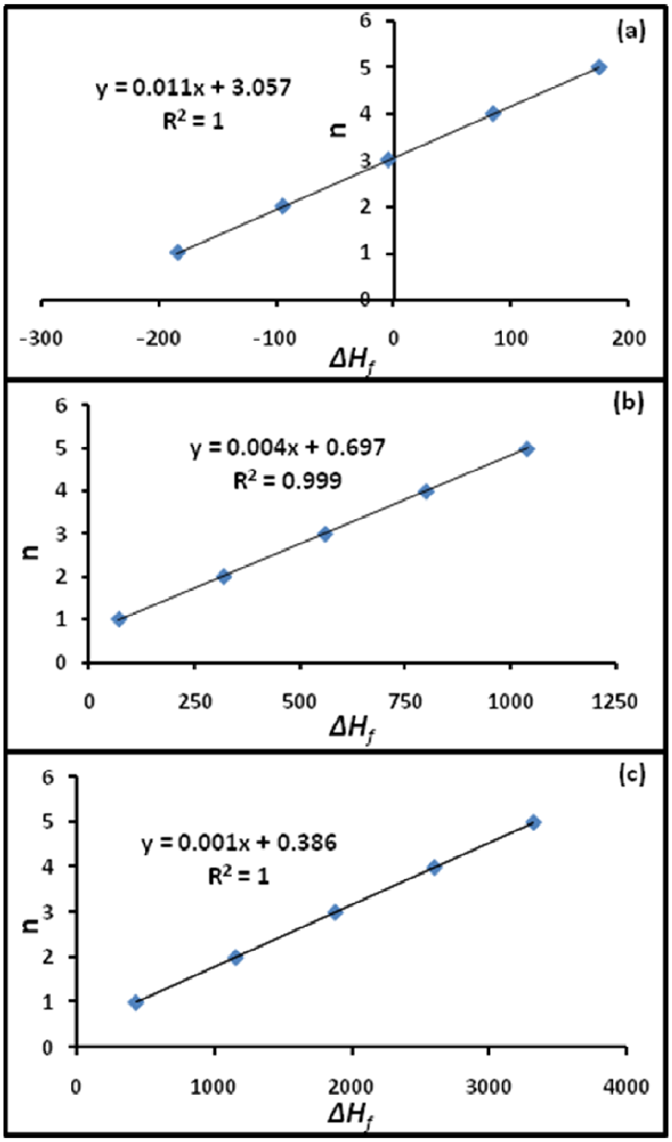


Fig. 4 Plots of linear fits computed at MP2/6-31G+(d)//B3LYP/6-31G(d) for number of monomer units (**n**) oligomers of (a) HTPB, (b) AHTPB and (c) GAP versus enthalpies of formations (ΔH_f) in kJ/mol.

HOMO − LUMO gap verses Sensitivity:

It is interesting to analyze the size dependence of the eigen value gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The estimated HOMO−LUMO gaps of HTPB and GAP can be compared with that of AHTPB in order to know their relative energetics and sensitivity. The energy gaps between frontier molecular orbital of studied oligomers are presented in Table 3. No correlation has been observed between HOMO-LUMO gap and number of repeating units (***n***) of the oligomers of the three polymers. However, best linear fits had been observed in literature for different conjugated polymers when HOMO−LUMO gaps have been plotted against inverse of number of repeating units (**1/*n***) of oligomers.[17,23-26] In our study, we have attempted to have the plots between **1/*n*** and HOMO–LUMO gap for the non-conjugated polymers HTPB, AHTPB and GAP. From the Figure 5, it certainly does not look like a linear dependence for all three plots in respect of oligomers. Such discrepancy seems to be due to the non-conjugated nature of the present polymers. Moreover, Bendikov et. al shown that the **1/*n*** extrapolation of HOMO-LUMO gaps fails to predict correct band gaps even for conjugated oligomers. Further, they have also concluded for conjugated polymers that the application of PBC/B3LYP/6-31G(d) is a very good method for predicting reliably the band gaps.[27] Therefore, we continued our study to determine the band gaps at PBC/B3LYP/6-31G(d) level of theory. The calculated band gaps for HTPB, AHTPB and GAP are found to be 6.85 eV, 5.83 eV and 6.14 eV, respectively. The HOMO–LUMO gap of HTPB is larger while that of GAP is smaller indicating the former is more stable or insensitive than the latter one (Figure 5). Similarly, the HOMO–LUMO gap of HTPB is even larger than that of AHTPB suggesting that the proposed azido HTPB is more energetic than inert polymeric binder HTPB as well as conventional energetic polymeric binder GAP. Based on the HOMO−LUMO gaps of these oligomers of polymeric binders concerned, the energetic trend of these polymeric binders should be HTPB < GAP < AHTPB. This indicates that substituent azido group exert different effect on HOMO–LUMO. As a result of more number of endothermic azido ($–N_3$) groups of AHTPB on HOMO−LUMO, the band gap decreases as compared to that of HTPB and GAP (Figure 5). The obvious insensitive or stability trend of these three polymers should be HTPB > GAP > AHTPB. The stability studied here for polymeric binders refers to the chemical processes with electron transfer or electron jump from valence band to conduction band.

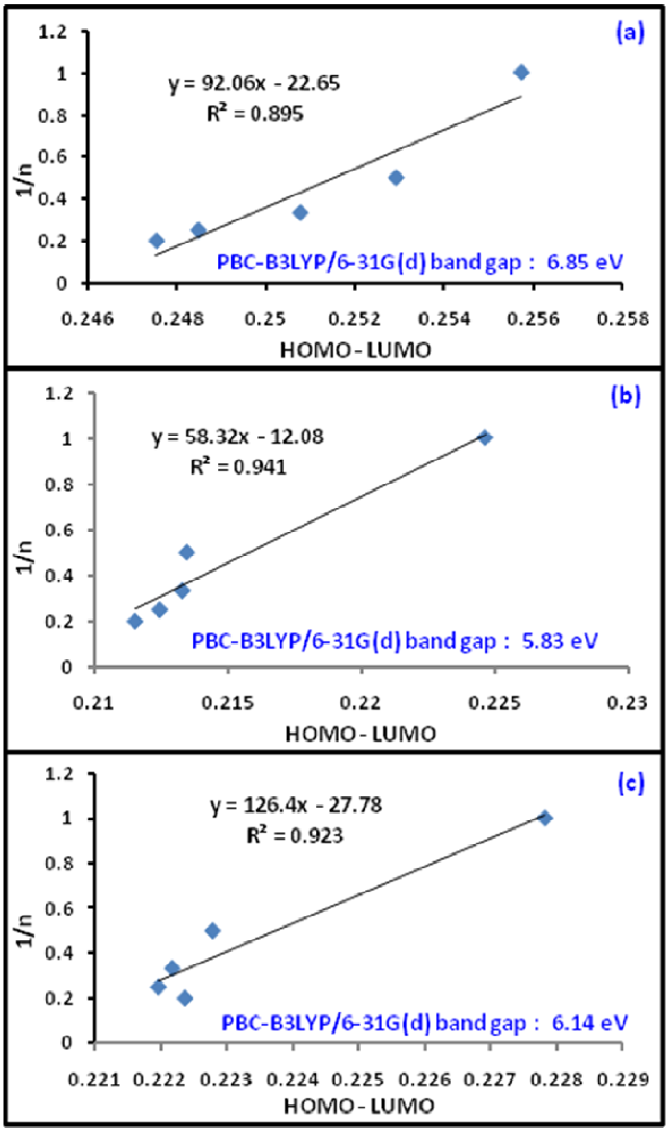


Fig. 5 Plots of linear fits computed at B3LYP/6-31G(d) for inverse of **n** (number of monomer units) verses HOMO - LUMO energies (eV) of oligomers: (a) HTPB, (b) AHTPB and **(c)** GAP (erg/cm^2).

Further, the global softness (S) has been computed from the energy (ε) values of HOMO and LUMO of five oligomers for all the three polymers (Table 4). It has been observed that the global softness of AHTPB increases gradually from monomer to pentamer as in the cases of HTPB and GAP. Therefore, global softness (S) values computed from equation 1 further indicate the feasibility of polymerization process of proposed AHTPB.

$$S = 1/(\varepsilon_{LUMO} - \varepsilon_{HOMO}) \qquad \ldots\ldots\ldots\ldots(1)$$

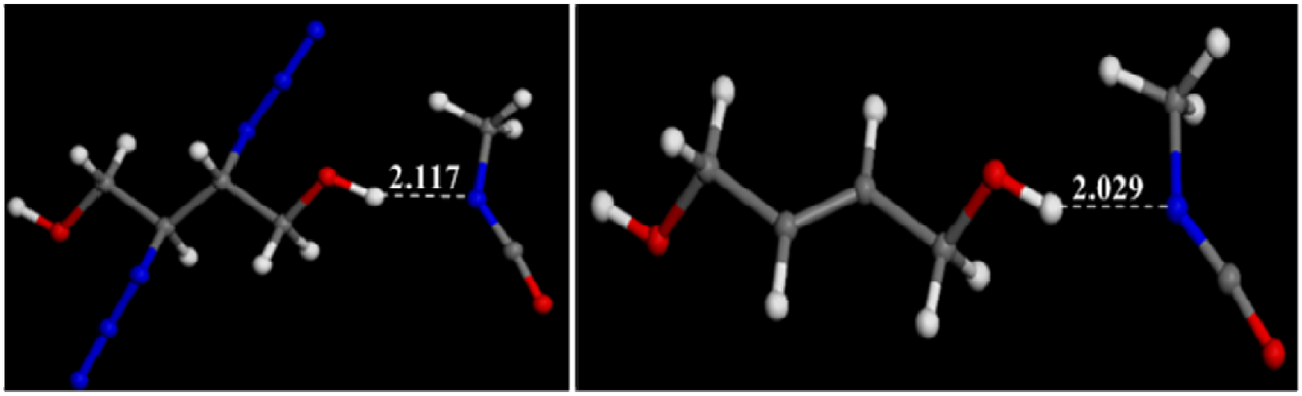
Table 3 Frontier molecular orbital gaps (HOMO−LUMO) of oligomers (n = 1 to 5) polymeric binders (values given in a.u.).

n	HTPB	AHTPB	GAP
1	0.25572	0.22464	0.22781
2	0.2529	0.21348	0.2228
3	0.25075	0.21331	0.22219
4	0.24846	0.21246	0.22198
5	0.24752	0.21154	0.22238

Table 4 Global softness (S) of oligomers (n = 1 to 5) polymeric binders (values given in a.u.).

n	HTPB	AHTPB	GAP
1	2.311658	2.28149	2.330513
2	2.413826	2.308403	2.269581
3	2.462508	2.315833	2.282584
4	2.483855	2.316584	2.318249
5	2.495072	2.320563	2.319809

The reactivity order of HTPB and AHTPB with isocyanate was further examined with the help of interaction energies towards exploiting their respective curing properties. To emulate the polymers HTPB and AHTPB, we have considered corresponding monomeric units towards their interaction with methyl isocyanate. Here, we have considered methyl isocyanate as a typical curing agent for the process of isocyanate based curing. The computed interaction energies accompanied with the corresponding geometries are shown in Figure 6. In this study, we have restricted to the first step of formation of urathene linkage i.e. abstraction of protan from hydroxy group through nitrogen lone pair as shown in the Figure 6. The monomer of HTPB forms a complex at a distance of 2.117 Å where as monomer of AHTPB at 2.029 Å. The interaction energies for the formation of complex of monomer of HTPB and monomer of AHTPB with methyl isocyanate were found to be −5.4 kcal/mol and −7.4 kcal/mol respectively. The computed results suggest that the monomer of AHTPB prefers to interact more strongly with the methyl isocyanate compared to that of HTPB. The reactivity predicted using the difference in interaction energies (IE) between isocyanate and monomer of HTPB and AHTPB suggests that the curing process of AHTPB should be greater than that of HTPB.



IE = -7.4 kcal/mol IE = -5.4 kcal/mol

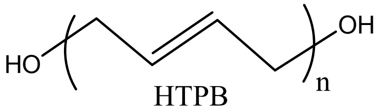
Fig. 6 B3LYP/6-31G(d) optimized geometries of complexes of monomers of HTPB and AHTPB with methyl isocyanate along with their electronic interaction energies computed with MP2/6-31G+(d).

Conclusions

In the present study, we have explored the computational methods towards the determination of enthalpies of formations of polymeric binders, hydroxyl-terminated polybutadiene (HTPB), azido, hydroxyl-terminated polybutadiene (AHTPB) and glycidyl azide polymer (GAP) by considering their respective oligomeric forms (monomer to pentamer). Band gaps have been determined from respective dimmers of three polymers employing periodic bond condition (PBC). In order to design the HTPB based energetic binder via azidation, we have examined azido HTPB through enthalpy of formation and frontier molecular orbital band gap calculations employing a combination of correlated molecular orbital and density functional theory. The gas phase enthalpies of formations are predicted with atomization reactions and the band gaps are estimated using HOMO-LUMO gaps. Our computed enthalpies of formations at MP2/6-31+G(d)//B3LYP/6-31G(d) level of theory using extrapolation method are found to be qualitatively reproduce the reported experimental enthalpies of formation values. The predicted enthalpy of formation value for AHTPB cannot be tested as experimental enthalpy of formation values for AHTPB are not available in the literature. The application of PBC/B3LYP/6-31G(d) method on dimers towards determining the band gaps suggested the relative stability or insensitivity trend of the studied polymers. The band gap studies shows that the proposed azido HTPB is relatively more sensitive than conventional HTPB as well as known energetic polymeric binder GAP. Interaction energies of monomer of HTPB and AHTPB with methyl isocyanate suggest that the AHTPB can be effectively curable than HTPB with isocyanate based curing agents. Considering the positive enthalpy of formation, curable nature and thermal stability, AHTPB is promising candidate of energetic polymeric binder, keeping the better mechanical properties of HTPB and is worth further investigations. A detailed and systematic study was performed with the intention to determine a sufficiently accurate but computationally affordable method for addressing structural and electronic properties of polymers. It is hoped that this study demonstrates both the ease and the potential pitfalls of calculating the heat of formations of polymeric binder systems. These results provide theoretical support for molecular design of novel high energetic polymeric binders and experimental synthesis.

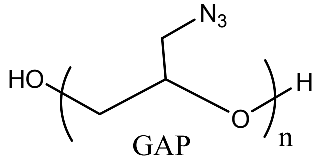
Computational Methodology

All geometries of oligomers were optimized using the B3LYP[28-30] density functional and the 6-31G(d) basis set.[31] Harmonic frequency calculations at the same level were used to validate the stationary points and to estimate thermodynamic corrections. Energies reported in this study are enthalpies obtained from normal mode analysis with the harmonic approximation. All quantum chemical calculations were performed using Gaussian 03, Revision E.01 program.[32] After proper minimum-energy structures were determined at B3LYP/6-31G(d), the enthalpy of formations of were determined using atomization reaction calculations for all species at MP2/6-31+G(d)//B3LYP/6-31G(d). The method of atomization reactions (equations 2−4) has been employed very successfully to calculate heat of formations from total energies obtained from *ab* initio calculations.[33,34]



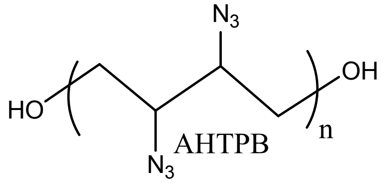
HTPB

$$\longrightarrow xC + yH + zO \quad \text{-------}(2)$$



GAP

$$\longrightarrow wC + xH + yO + zN \quad \text{-------}(3)$$



AHTPB

$$\longrightarrow wC + xH + yO + zN \quad \text{-------}(4)$$

The energies corresponding to the HOMO and LUMO were extracted from the final equilibrium geometries of each oligomer. Thereafter, Δ*E*, which is the energy difference between the HOMO and LUMO, was calculated for each oligomer. The band gaps for polymers using periodic boundary condition (PBC) have been computed as suggested in reference 27. The optimizations using PBC were carried out by considering dimers of polymers without any symmetry constraints. It was shown that band gaps predicted for The procedure employed here for the determination of heat of formation calculations has been proved to be a very successful procedure in previous studies.[33,34] The theoretical enthalpy of formation at 298 K is calculated using the following atomization reactions

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Supplementary Information Available

B3LYP/6-31G(d) and PBC/B3LYP/6-31G(d) optimized Cartesian coordinates of all stationary points, including corresponding charge and multiplicity are available in the supplementary data.

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Graphical Abstract

On Calculating Polymeric Binders' Enthalpy of Formations and Band Gaps with Computational Methods

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Determinations of enthalpy of formations and band gaps of polymeric binders have been considered for the linear fit extrapolation and PBC techniques, respectively, which suggest the azido HTPB can be a potential energetic binder in explosive compositions.