Terminal Functionalized Hydroxyl-Terminated Polybutadiene: An Energetic Binder for Propellant

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ABSTRACT: We report the functionalization of hydroxyl terminated polybutadiene (HTPB) backbone by covalently attaching 1-chloro-2, 4-dinitrobenzene (DNCB) at the terminal carbon atoms of the HTPB. The modification of the HTPB by the DNCB does not alter the unique physico–chemical properties and the microstructure of the parent HTPB. IR, ^{1}H-NMR, ^{13}C-NMR, size exclusion chromatography (SEC) and absorption spectroscopy studies prove that the DNCB molecules are covalently attached to the terminal carbon atoms of the HTPB. The π electron delocalization owing to long polymer chain, strong electron withdrawing effect of the DNCB molecule are the major driving forces for the covalent attachment of the DNCB at the terminal carbon atom of the HTPB. We are the first to observe the existence of intermolecular hydrogen bonding between the terminal hydroxyl groups of the HTPB. IR study shows that the attached DNCB molecules at the terminal carbon atoms of the HTPB breaks the intermolecular hydrogen bonding between the HTPB chains and forms a hydrogen bonding between the NO_2 groups of the DNCB and the OH groups of the HTPB. Absorption spectral study of the modified HTPB indicates the better delocalization of π electron of butadiene due to the strong electron withdrawing effect of the DNCB molecules. Theoretical calculation also supports the existence of hydrogen bonding between the OH and NO_2 groups. Theoretical calculation shows that the detonation performance of both the DNCB and the HTPB-DNCB are promising. HTPB-DNCB is the new generation energetic binder which has potential to replace the use of HTPB as binder for propellant. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 732–741, 2009

Key words: functionalization of polymers; polybutadiene; FTIR; intermolecular hydrogen bonding; energetic binder

INTRODUCTION

The binders for composite propellant are typically cross-linked polyurethanes providing a matrix to bind the solid energetic materials together with the plasticizer. Binder helps the friendly processing of the energetic materials and provides the required mechanical strengths to the final composition of the propellant.[1–3] Mixture of nitrocellulose and nitroglycerine was one of the earliest binder used in the composite propellant.[4] The modern high performance composite propellants employ hydroxyl-terminated polybutadiene (HTPB) as binder because of its unique physico–chemical properties such as excellent flow characteristics and storage capacity compared to other known binders.[5–7] Because of the outstanding mechanical properties of polyurethane made from the HTPB, HTPB has been used in the field of explosives since 1989 as a crosslinkable prepolymer. Several commercially available explosives are qualified with the HTPB in propellant formulation.[8] The shock responses of the HTPB polyurethane with energetic materials and without energetic materials have been studied thoroughly by several authors.[9–11] The excellent shock absorbing capacity of the HTPB polyurethane drastically reduces the sensitivity and vulnerability of the explosive materials. HTPB based polyurethanes have also been studied in the literature by several authors for the separation of organic compounds,[12] for selective adsorption of proteins[13] and for selective gas transport properties.[14] Recently, HTPB has been successfully used for the fabrication of elastic conducting polymer microparticles with core-shell structure.[15]

Either the anionic or free radical polymerization methods are used to synthesize the HTPB polymer. The polymerization conditions like type of initiator, solvent, polymerization temperature and polymerization time vary the extent of polydispersity of molecular weight and functionality. In case of the HTPB three different types of microstructures (e.g., cis, trans, vinyl) are possible because of the probability of addition of monomer in three different ways. The quantity of microstructure present in HTPB sample dictates the flow characteristics of the sample

and the mechanical properties of the corresponding polyurethane. For example, the viscosity of the HTPB increases with increase in vinyl content and the mechanical properties such as tensile strength, % elongation of the propellant show significant improvement with increasing trans content and decreasing vinyl content.[16,17] Thus, a large number of efforts have been made in the literature on the determination and evaluation of the microstructure of the HTPB using various techniques such as IR, ^{1}H-NMR, ^{13}C-NMR etc.[18–21]

Although the HTPB has the excellent physical properties to serve as a binder and reduce the vulnerability of explosive charges but it has some unavoidable problems. It is inert in nature; HTPB "dilutes" the explosive by reducing the overall energy output and the performance of the composition. Theoretically HTPB can load 92% solid energetic materials but rest 18% in the propellant formulation is inert binder which reduces the overall energy output of the propellant. Although the inert binders have been employed effectively in the explosive composition, however, there is a need and challenge for the development of energetic binder by introducing energetic functionality. Several energetic binders such as glycidyl azide polymer, poly (3-nitratomethyl-3-methyloxetane), poly (glycidylnitrate), polyvinyl nitrates etc. have been developed and reported in the literature.[22–24] However, these binders have several limitations for their use in the propellant formulation. Therefore, till now HTPB is the first and best choice for propellant formulation despite of the availability of these new energetic binders. Thus, it is evident that there is a tremendous scope to develop energetic HTPB by introducing energetic functionality on it without destroying its excellent physico–chemical properties. A considerable number of efforts have been put forward in the literature to modify the HTPB by attaching energetic functionality into the backbone.[25–27] The HTPB backbone has been nitrated by two different reaction pathways: the classical method which employs a nitromercutation-demercutation route, or alternatively, by epoxidation of HTPB and the nitrating with dinitrogen pentaoxide. It has been observed that up to 10% nitration on the HTPB backbone gives a good balance of energy output, mechanical properties and miscibility with energetic plasticizers.[25] The grafting of energetic polymers such as poly (glycidyl azide) onto HTPB has also been tried in the literature.[26] Recently, iron was coordinately linked to the HTPB backbone to enhance the burn rate of the composite solid propellant.[27] Unfortunately none of these efforts are able to replace the use of HTPB in propellant due to not adequate advantages achieved by these efforts. In this article, we are reporting the modification of HTPB backbone

TABLE I
Various Characteristic Data of the HTPB and the HTPB-DNCB

Various Characteristics	HTPB	HTPB-DNCB
Number average molecular weight ($\overline{M_n}$)	5210	5600
Poly dispersity index (PDI)	2.53	2.53
Viscosity (cp) at room temp. (27°C)	2320	2170
Hydroxyl value (mg KOH/gm)	42	39
Microstructure (%) (cis, trans, vinyl)[a]	29, 64, 7	25, 70, 5

[a] Calculated from ^{1}H-NMR spectra.

by covalently attaching an energetic molecule 1-chloro-2, 4-dinitrobenzen at the terminal carbon atoms of the HTPB. We have characterized the functionalized HTPB using IR, NMR, and UV-vis etc. and calculated their detonation performance theoretically.

EXPERIMENTAL SECTION

Materials

The hydroxyl-terminated polybutadiene (HTPB) used in this work was prepared by free radical polymerization using hydrogen peroxide as initiator which was received form HEMRL Pune, India as a gift sample. HTPB sample was dried in a rotary evaporator at 80°C under continuous vacuum to remove the residual moisture. Moisture free HTPB sample was stored in a closed vessel after thorough nitrogen gas purging. The HTPB sample was characterized by various techniques and the data were listed in Table I. Sodium hydride (NaH) and 1-chloro-2, 4-dinitrobenzene were purchased from LOBA chemical, India and used as received. All the solvents (chloroform, tetrahydrofuran, dichloromethane) were dried and distilled before they were used. NMR solvents were obtained from Merck, India.

Functionalization of HTPB by DNCB

3.345 gm (0.062 mol; considering 54 as a molecular weight of HTPB repeat unit) of moisture free HTPB was taken in 10 mL of dichloromethane solvent in a three neck round bottom flask fitted with a guard-tube and continuous nitrogen purging. After completely dissolving the HTPB in dichloromethane solvent by stirring using a magnetic stirrer, 0.223 gm (0.01 mol) of NaH was added to the HTPB solution in presence of continuous nitrogen gas purging. The mixture was stirred for 30 min and then the
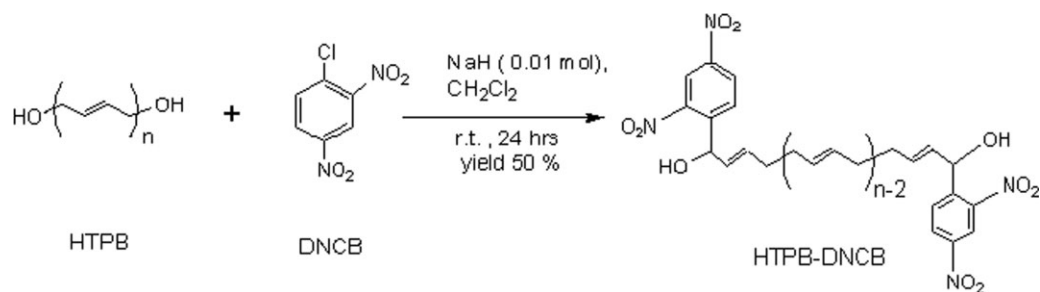
Scheme 1 Terminal functionalization of HTPB by DNCB.

1-chloro-2,4-dinitrobenzen (0.205 gm, 0.001 mol) was added to the reaction mixture. The stirring was continued for another 3 h in presence of nitrogen gas purge and then stirring was continued for overnight without nitrogen gas. The pale yellow color of the initial reaction mixture was disappeared after overnight stirring and a dark reddish brown color appeared. The solvent was removed at 50°C in rotary evaporator. The resulting compound was washed thoroughly and repeatedly with methanol followed by hexane to remove the traces of the NaH, unreacted DNCB and excess HTPB. The purity of the resulting sample was checked by thin layer chromatography (TLC) using 3 : 2 (V/V) mixture of hexane and ethylacetate as a solvent. The purified resulting compound (HTPB-DNCB) was fluidic in nature as HTPB and the yield of the reaction was 50%. We have not observed any side products; however, moderate quantity of HTPB was unreacted in nature which was removed by repeated washing using methanol and hexane. The reaction scheme for the modification of HTPB is presented in Scheme 1.

Characterization of the functionalized HTPB

The molecular weights and molecular weight distributions of the samples (HTPB and HTPB-DNCB) were determined by SEC using a water 1515 isocratic HPLC pump connected to three water styragel HR1, HR3, and HR4 columns and a waters 2414 refractive index detector at room temperature (25°C). THF was used as eluent with a flow rate of 1 mL/min and narrow polystyrene standards having peak molecular weights (MP) 860, 1800, 3600, 8500, 19,100, 43,400, 76,300, and 139,400 were used for calibrating the GPC. Breeze software was used to calculate the calibration curve as well as data of the samples. FTIR spectra of the HTPB and the HTPB-DNCB were recorded on a JASCO-5300 Fourier spectrometer (FTIR) with 4 cm^{-1} resolution. The spectra were taken using the neat samples in KBr crystal. The ^{1}H-NMR and ^{13}C-NMR of the samples were recorded on a Bruker 400 MHz spectrometer using CDCl$_3$ as a solvent. The UV-visible absorption spec-

tra of the dilute solution of the sample in THF solvent were recorded on a Cary-100Bio (VARIAN) spectrophotometer. The hydroxyl values of the samples were determined by acetylation method using pyridine and acetic anhydride as a reagent mixture.[28] The viscosity was determined using Brookfield viscometer (DV-III Ultra model).

Computational details

All the quantum mechanical calculations were performed with the Gaussian 03 program package.[29] The Becke three-parameter hybrid (B3) functional was used along with Lee-Yang-Parr (LYP) correction.[30,31] The 6–31g* basis set is employed in all calculations reported here. Vibrational frequencies were calculated to characterize the stationary points and zero-point vibrational energies (ZPVE) correction.

RESULTS AND DISCUSSION

Modification of HTPB with DNCB

We have modified the HTPB by covalently attaching the 2, 4 dinitrochlorobenzene (DNCB) in the polymer backbone. DNCB is an energetic molecule as evident from theoretical calculation which is discussed in the later section. Therefore, we could expect that the modified HTPB (HTPB-DNCB here after) would be an energetic binder system. In the later section we have carried out theoretical analysis of the HTPB-DNCB which shows that the modified HTPB is an energetic binder indeed. The covalent attachment of the DNCB on to the HTPB backbone is carried out using NaH as a catalyst in CH$_2$Cl$_2$ solvent by taking appropriate moles of the HTPB and the DNCB. After a careful and thorough purification of the HTPB-DNCB compound is subjected to various characterization processes. Because there is no as such functional group except the terminal hydroxyl groups in the HTPB backbone, therefore one can argue that the DNCB molecule is not covalently attached in the HTPB backbone rather the final product is nothing but a physical mixture of HTPB and DNCB. We believe that the catalyst NaH
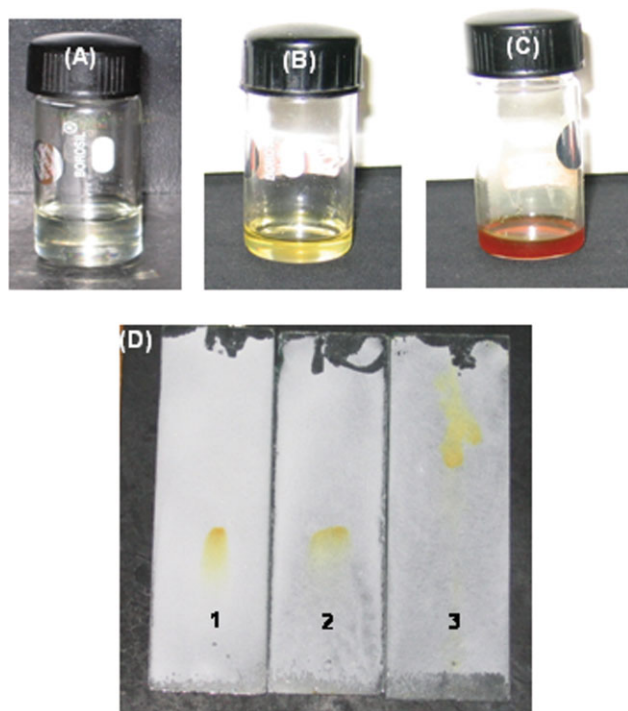
Figure 1 Photographs of (A) parent HTPB, (B) the product of the reaction between HTPB and DNCB without NaH as a catalyst in the reaction (control experiment), (C) the modified HTPB-DNCB sample and (D) the TLC spots of the above samples; 1, 2, and 3 correspond to A, B, and C, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

plays an important role for the covalent attachment of DNCB molecule in the HTPB backbone. The detail mechanism will be explained in the next section. We

have carried out a control reaction of HTPB and DNCB in similar mole ratio and in similar reaction condition without NaH, and then subjected to the similar purification process. DNCB is a pale yellow color molecule and HTPB is a colorless compound. Hence only if DNCB is attached covalently then only we would expect DNCB colour in the final product. From Figure 1, it is clear that if we use NaH as catalyst in the reaction then only we get the color product as well as the separate clear spot different from the HTPB in the TLC plate, otherwise the final product is almost colorless and gives a spot in the same place as HTPB in the TLC plate.

We have characterized the HTPB-DNCB sample using FTIR, ^{1}H and ^{13}C-NMR. The IR spectra of HTPB-DNCB compound along with HTPB shown in Figure 2. The spectrum of HTPB-DNCB shows the characteristic broad stretching frequency at around 3449 cm^{-1} due to terminal OH of the HTPB,[32] frequency at 3074 cm^{-1} represents the aromatic C—H stretch, 2916 cm^{-1} and 2847 cm^{-1} owing to the aliphatic C—H stretching. The characteristic peak at 1639 cm^{-1} belongs to C=C bonds of HTPB, at 1608 cm^{-1} due to C=C stretch of aromatic ring. The 1539 cm^{-1} and 1344 cm^{-1} peaks are the NO$_2$ symmetric and asymmetric stretch. The sharp peaks at 966 cm^{-1} and 912 cm^{-1} and 720 cm^{-1} are due to 1,4 trans, 1,2 vinyl, and 1,4 cis microstructure of HTPB, respectively.[16] Hence, the presence of OH stretching in the IR spectrum (Fig. 2) of the HTPB-DNCB clearly proves that the modification of the HTPB backbone by DNCB does not kill the availability of the free OH groups. The hydroxyl value obtained in
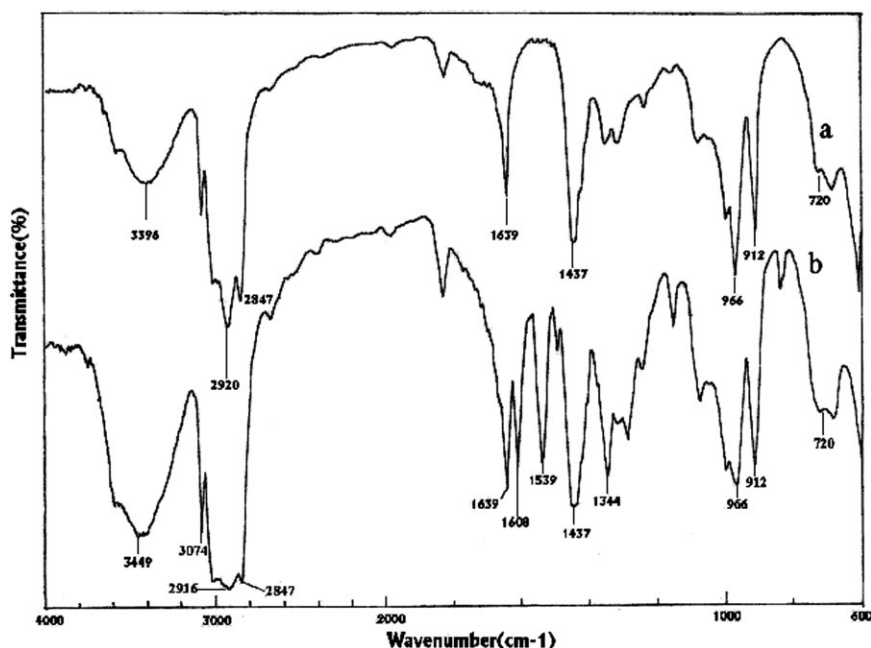

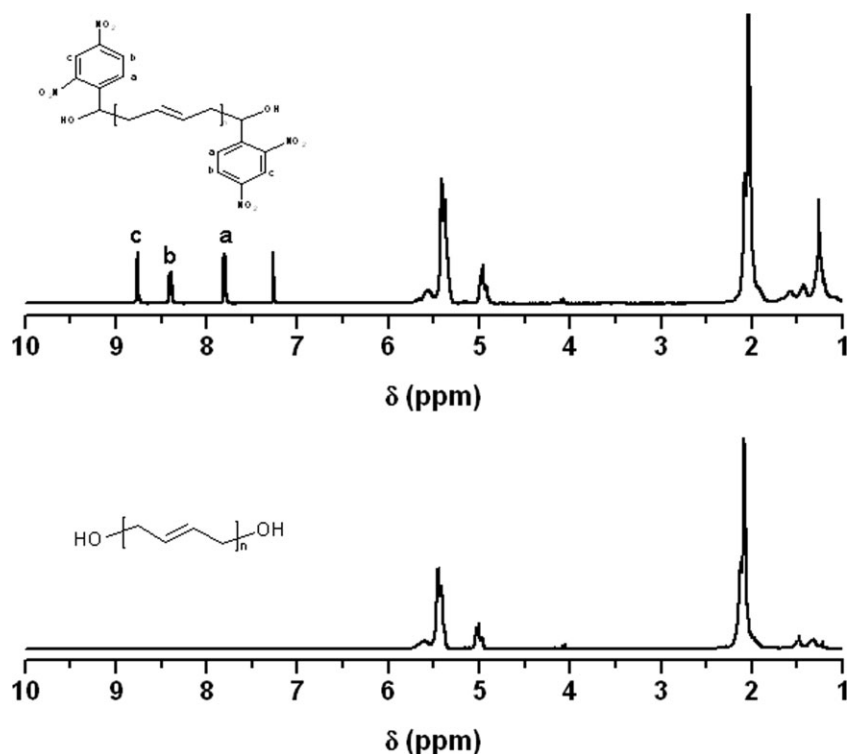**Figure 2** FTIR spectra of the (a) HTPB and (b) HTPB-DNCB.

Figure 3 Proton NMR of the HTPB and the HTPB-DNCB.

both HTPB and HTPB-DNCB sample is almost similar (Table I) also attributes that free OH groups are available in the HTPB-DNCB for propellant formulation. The presence of all microstructure frequencies and C=C frequency in the HTPB-DNCB (Fig. 2) indicate that the modification has not affected the microstructure of the HTPB backbone. The ^{1}H-NMR spectra of HTPB and HTPB-DNCB compound along with the chemical structures and peak assignments are presented in Figure 3. The signals at δ 7.78 (d, 2H), 8.37 (d, 2H), and 8.75 (s, 2H) are due to aromatic region of DNCB segment. This proves the presence of DNCB in the HTPB backbone. The other chemical shift regions of the HTPB-DNCB compound at δ = 1.2–1.4, 2–2.1, and 4.9–5.4 are exactly identical with the parent HTPB.[20,21] This reveals that in the HTPB-DNCB sample, the microstructure of HTPB has not been changed. The microstructure data calculated from ^{1}H-NMR are presented in Table. I also supports our argument. Figure 4 shows the ^{13}C-NMR spectra of the HTPB-DNCB and the HTPB in CDCl$_3$ solvent. The peaks in the δ 25–43 region corresponds to aliphatic carbons of HTPB and the peaks at δ 114–142 region belongs to olifinic carbons of HTPB.[18] Because both olifinic carbons and aromatic carbons show peaks in the similar region (δ 114–142), therefore it is difficult to find out peaks for aromatic carbon due to DNCB moiety in the HTPB-DNCB sample. However, a careful look at

the HTPB-DNCB spectrum shows the few extra peaks at 121.1, 127.4, 133.2, and 133.8. These peaks are absent in the HTPB indicates the presence of DNCB in the modified HTPB sample. Thus, we can conclude that FTIR, ^{1}H-NMR, and ^{13}C-NMR analysis demonstrate the covalent attachment of DNCB onto the HTPB back bone. The viscosity of the HTPB has not been changed after the attachment (Table I)
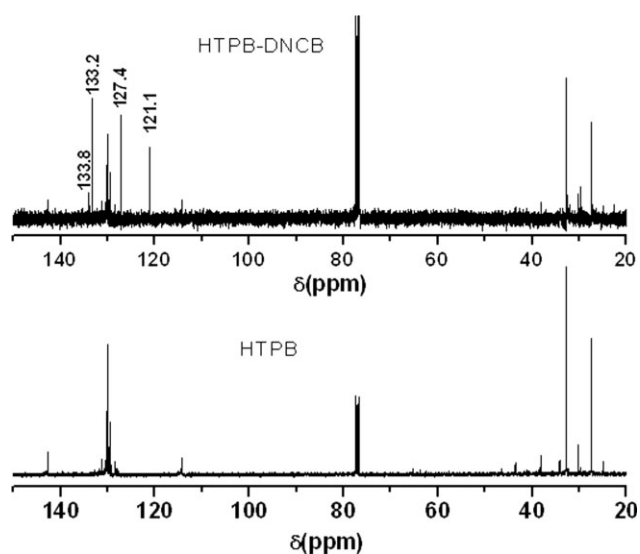

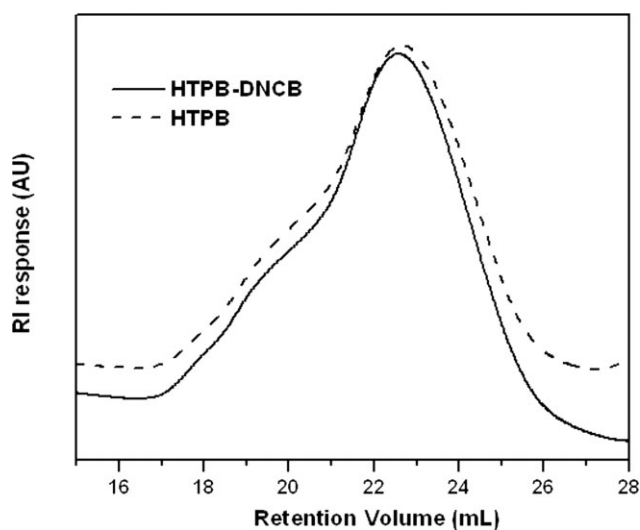**Figure 4** ^{13}C-NMR of the HTPB and the HTPB-DNCB.

Figure 5 Size Exclusion chromatography traces of the parent and the modified HTPB samples.

indicates that the flow characteristic of the HTPB-DNCB remains same as HTPB. Hence, the HTPB-DNCB can load the similar quantities of energetic materials as the HTPB. Thus we summarize that modification of the HTPB is successful without disturbing the microstructure, other essential and unique physico–chemical properties of HTPB.

Proposed mechanism for the HTPB-DNCB formation

The SEC traces of the HTPB and the HTPB-DNCB are presented in the Figure 5. Both the traces are similar in nature. The calculated number average molecular weight ($\overline{M_n}$) from these traces are 5210 and 5600 for the HTPB and the HTPB-DNCB, respectively. The polydispersity index (PDI) for both the samples are 2.53 (Table I). Similar type of SEC traces, identical PDI and almost identical $\overline{M_n}$ values indicate that the HTPB structure is retained after the covalent attachment of the DNCB onto the HTPB backbone. Because we have not observed any peaks for small molecule in the HTPB-DNCB sample (Fig. 5), thus it can be concluded that the DNCB is covalently attached to the polymer backbone. However, there is an increase of $\overline{M_n}$ by $\sim$ 400 in case of the HTPB-DNCB. This attributes that probably only two DNCB units have attached to the HTPB backbone (Scheme 2). Each DNCB unit contributes 167; hence two contributes nearly 334 which is close to 400. Based on this observation we proposed the following mechanism.

The strong base NaH abstracts the proton from the terminal OH of the HTPB and generates oxy anions at the terminal ends of the HTPB. Because oxy anions are not stable, thus they are easily converted to allyl anions by abstracting protons from
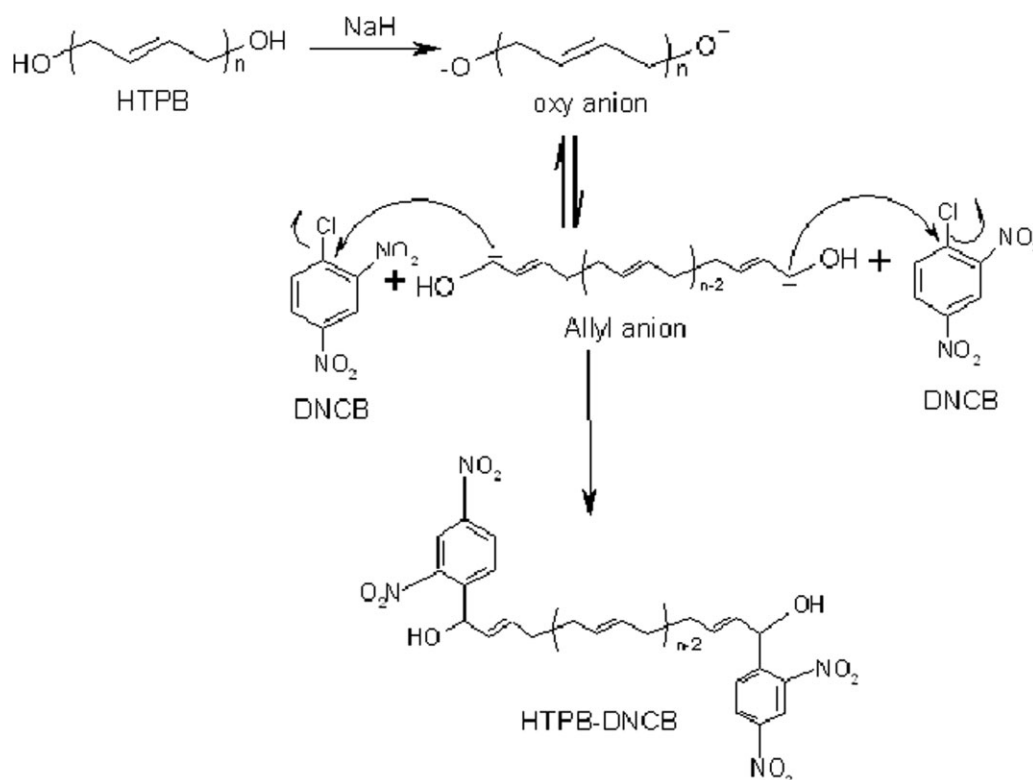
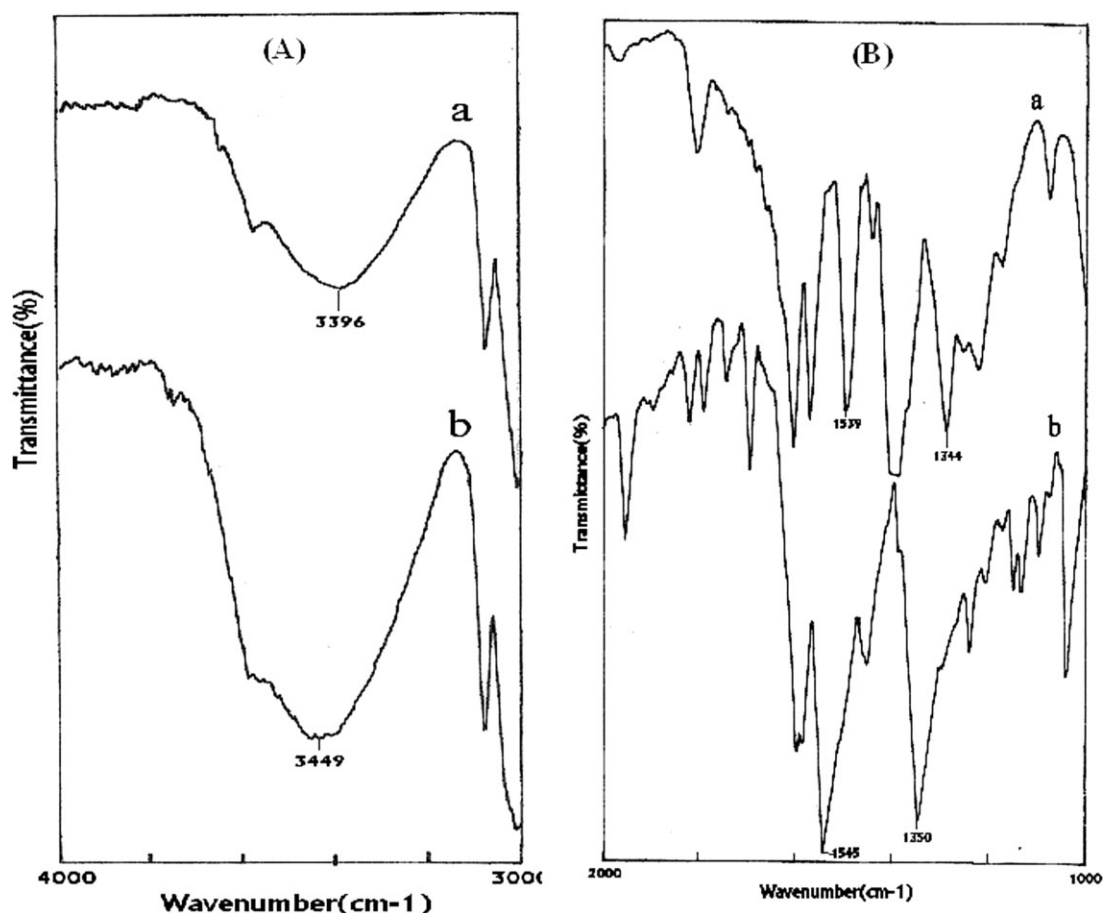**Scheme 2** Proposed mechanism for the HTPB-DNCB formation.

Figure 6 (A) FTIR spectra of (a) HTPB and (b) HTPB-DNCB, (B) FTIR spectra of (a) HTPB-DNCB and (b) DNCB.

the neighboring carbon atoms. The ally anion is stable due to the butadiene π electron delocalization through the resonance stabilization which arises because of the long conjugation of the HTPB backbone. Hence the terminal carbons of HTPB act as nucleophile. Because of the strong electron withdrawing effect of —NO_2 groups of the DNCB, the Cl^- of DNCB acts as a very good leaving group. Therefore the DNCB molecule can easily attach at the two ends of the HTPB. Our GPC data presented in Figure 5 and the increase of $\overline{M_n}$ values (Table I) in case of HTPB-DNCB clearly proves that two DNCB functional groups are attached in the chain. Our FTIR, NMR, and hydroxyl value results discussed in the previous section clearly proves that the presence of free OH at the two terminals of the HTPB and double bond in the HTPB backbone. Though our proposed mechanism (Scheme 2) suggests the attachment of the DNCB molecules at the two terminal carbon atom of each HTPB chain; however, the obvious question arises that what is the proof of the terminal attachment? not the attachment inside the HTPB chain. We believe that the DNCB molecules are attached at two terminal carbons of HTPB as presented in the Scheme 2. To support our

argument we have analyzed FTIR data carefully presented in the Figure 2. We have zoomed the two regions; 3000–4000 cm^{-1} and 1000–2000 cm^{-1}, of Figure 2 and presented in Figure 6 to look into the any observable changes of the stretching frequencies in these two regions. The terminal OH of the HTPB shows stretching at 3396 cm^{-1} which is much lower than the expected stretching of the free OH at 3600 cm^{-1} or higher than 3600 cm^{-1}.[33] This reveals that in the HTPB a strong intermolecular hydrogen bonding between the OH groups of different polymer chains exists. Surprisingly, the HTPB-DNCB sample shows OH stretching at 3449 cm^{-1} [Fig. 6(A)]. This indicates that DNCB molecule is breaking the intermolecular hydrogen bonding between the terminal hydroxyl of the HTPB chains and as a result OH stretching for the modified HTPB observed at higher wavenumber than the parent HTPB. From the Figure 6(B), it is clearly visible that both symmetric and asymmetric stretching of NO_2 groups in the HTPB-DNCB sample are moved to lower wavenumber than the DNCB molecule. This attributes the formation of hydrogen bonding between the OH groups of the HTPB and the NO_2 groups of the DNCB. Thus the existence of the
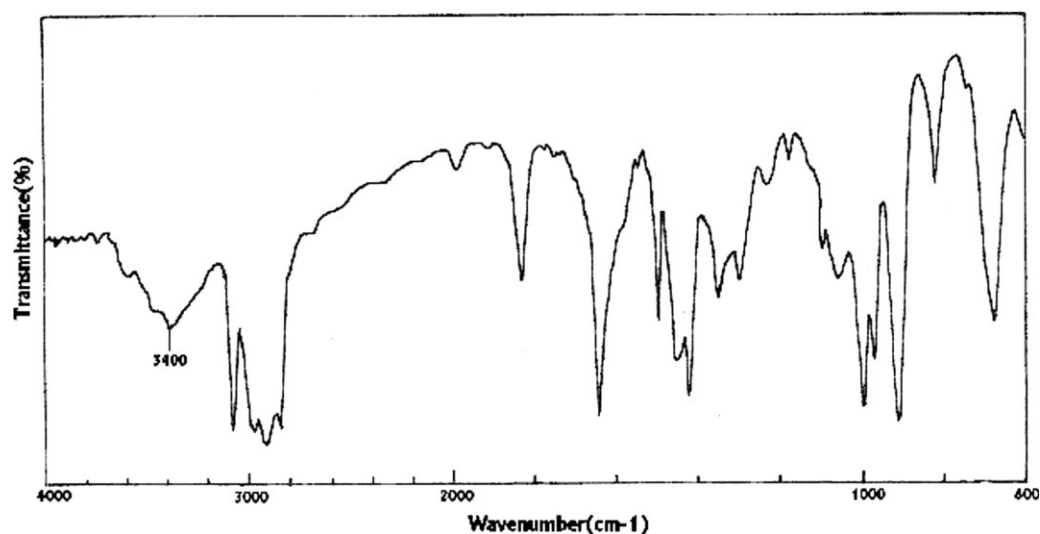
Figure 7 FTIR spectrum of HTPB-PCA.

hydrogen bonding between terminal OH and NO_2 and breaking of intermolecular hydrogen bonding are proved from the IR study. Therefore, for successful hydrogen bonding between NO_2 and OH, the DNCB molecules have to be in the adjacent carbon atoms of the OH groups. Thus the terminal attachment of the DNCB is expected and obvious. Hence our proposed mechanism given in the Scheme 2 is justified. We have carried out a control experiment for hydrogen bonding between NO_2 and OH. We have modified HTPB by reacting with parachloroaniline (PCA) and the FTIR spectrum of HTPB-PCA is presented in Figure 7. The OH stretching for this sample is observed at 3400 cm^{-1} which is exactly similar to HTPB. The PCA molecule does not have any functional group at the ortho position of the aromatic ring. Hence the PCA molecule attached to terminal carbon atoms of the HTPB could not take part in the hydrogen bonding with the terminal hydroxyl groups of the HTPB. Therefore the OH stretching (3400 cm^{-1}) of the HTPB-PCA sample is similar to the HTPB sample. This observation clearly showed that the functional group at the ortho position of the aromatic ring is absolutely necessary for the hydrogen bonding. Hence our control experiment clearly demonstrates that the NO_2 group of DNCB forms a hydrogen bonding between NO_2 and OH and breaks the intermolecular hydrogen bonding of the terminal OH of the HTPB chains. From our theoretical calculation (discussed in the later section) we have obtained the energy minimized structure which also shows the efficient hydrogen bonding between OH and NO_2 groups.

Absorption spectroscopy

The electronic absorption spectra of DNCB, HTPB, and HTPB-DNCB compound are studied from their dilute solution in THF solvent. The absorption spectra of the all the three compounds in THF solvent are shown in the Figure 8. HTPB shows $\pi \rightarrow \pi^*$ transition peak of cis microstructure at 230 nm and $\pi \rightarrow \pi^*$ transition peak of trans microstructure at 280 nm. DNCB molecule has a sharp distinct peak at 252 nm and a broad shoulder at 350 nm. HTPB-DNCB shows three distinct sharp peaks at 252 nm, 294 nm, and 365 nm. The 252 nm peak in the HTPB-DNCB attributes the presence of the DNCB moiety in the HTPB backbone. The peak at 294 nm in the HTPB-DNCB corresponds to the $\pi \rightarrow \pi^*$ transition of trans microstructure of the HTPB. Therefore, from the Figure 8, it is evident that the $\pi \rightarrow \pi^*$ transition of HTPB backbone has been red shifted from 280 nm
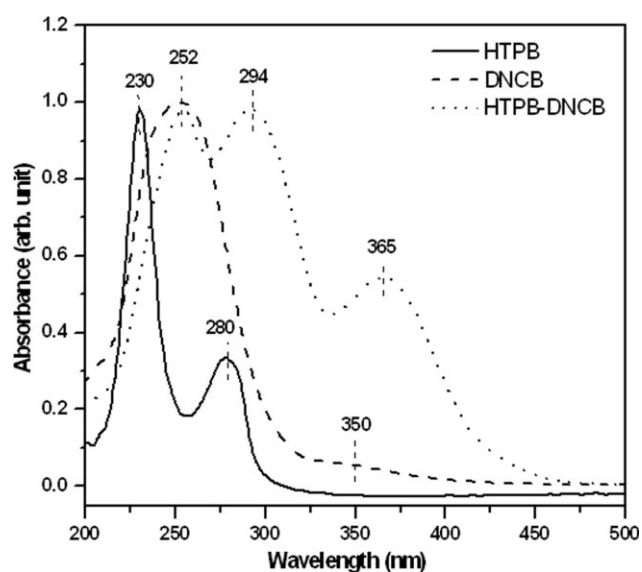

Figure 8 Absorption spectra of the HTPB, DNCB and HTPB-DNCB from their dilute solution in THF.

to 294 nm after the modification of the HTPB backbone with the DNCB molecules. This 15 nm bathochromic shift is clearly due to the strong electron withdrawing inductive and resonance effect of $-NO_2$ groups of the DNCB. Because of the strong electron withdrawing nature of the DNCB, the π electrons of the butadiene are more delocalized in case of the HTPB-DNCB compared to the HTPB. Hence, we have observed a 15 nm red shift of the $\pi \rightarrow \pi^*$ transition peak. This observation once again provides the evidence for the existence of covalent linkage between the DNCB and the HTPB. The strong absorption at 365 nm in the HTPB-DNCB is the red shifted 350 nm peak of the DNCB (Fig. 8). This red shift and strong absorption arise because of the extended conjugation of DNCB when it is attached to the HTPB backbone. The absence of $\pi \rightarrow \pi^*$ transition of the HTPB cis microstructure at 230 nm in the HTPB-DNCB sample (Fig. 8) attributes that DNCB preferably attaches to those chains where cis microstructure is less.

Theoretical calculation

We have carried out theoretical calculation on the DNCB and the HTPB-DNCB molecules to look into their potential as energetic materials. Various parameters such as density, detonation pressure (P_D) and velocity of detonation (VOD) of these molecules are calculated and presented in Table II. Detonation data for well known explosive such as trinitrotoluene (TNT)[1] are also listed in the Table II for comparison. For the simplicity of the calculation in the case of HTPB-DNCB, we have considered only one repeat unit of HTPB with two DNCB molecules attached to the terminal carbon atoms. Figure 9 represents the energy minimized structure of the HTPB-DNCB. The presence of trans conformer and hydrogen bonding between the NO_2 and OH group in the HTPB-DNCB are clearly visible in the energy minimized structure presented in Figure 9. Hence, both our theoretical calculation and experimental results obtained from IR, NMR, and UV are matching well and suggest the presence of hydrogen bonding and trans microstructure in the HTPB-DNCB. Table II data reveals that the densities of DNCB and HTPB-DNCB are comparable with the TNT. The detonation perform-
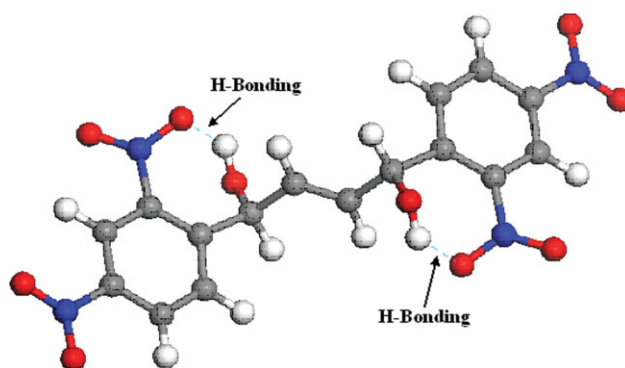

Figure 9 Energy minimized stable structure of the HTPB-DNCB. Energy minimization was carried out considering single repeat unit. Structure shows the presence of trans conformation and hydrogen bonding. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ance of DNCB and HTPB-DNCB are also comparable to that of TNT. The velocity of detonation for both the compounds are almost similar to TNT. In the case of HTPB-DNCB compound the detonation pressure is bit lower than TNT. However, it is important to note that HTPB-DNCB is meant for binder application, so the extra energy supplied by this to the propellant system would be added energy to the systems; therefore the obtained detonation performance is sufficient enough.

CONCLUSION

We have functionalized the HTPB backbone by covalently attaching the DNCB molecule without destroying the unique physico–chemical properties such as fluidity, microstructure and the presence of free hydroxyl group at the terminal of the parent HTPB. Our studies show that the DNCB molecules are attached at the terminal carbon atoms. We have observed the presence of intermolecular hydrogen bonding in the parent HTPB. However, after the functionalization of the HTPB by DNCB, the intermolecular hydrogen bonding breaks due to the formation of hydrogen bonding between the NO_2 and the OH groups. The HTPB-DNCB have more delocalized π electron than parent HTPB. Theoretical study shows that the HTPB-DNCB has moderate detonation property. Hence the HTPB-DNCB may widen the scope and application as a promising energetic binder in solid rocket propellants and enhance the energetic characteristics of the propellant.

TABLE II
Detonation Performance Data

Molecule	Density (g/cc)	Detonation pressure (G Pa)	Velocity of detonation (Km/s)
DNCB	1.60	15.06	6.05
HTPB-DNCB	1.45	13.37	5.88
TNT	1.64	19.78	6.90

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