


# On Structure and Secondary Linkages in Polymers Based on Glycidyl Azide Polymer and Diisocyanate

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## ABSTRACT

Polymers based on glycidyl azide polymer (GAP) and isocyanate present molecular structures dependent on NCO/OH molar ratio and diisocyanate reactivity. In this study, GAP polymers are obtained from a reaction with aromatic (toluene diisocyanate, TDI) or aliphatic (isophoronediiisocyanate, IPDI) diisocyanates, varying the NCO/OH molar ratio from equimolar to 2.5. The increment in NCO/OH molar ratio increases the gel fraction in GAP/TDI polymers up to 90 wt%, along with a progressive growth in their glass transition temperature ( $T_g$ ), which rises 10 °C from NCO/OH equimolar to 2.5. In opposition, in the GAP/IPDI polymers, the maximum gel fraction is 20 wt%, and the  $T_g$  value practically does not change in NCO excess. Infrared spectroscopy shows the predominant presence of urethane groups in polymers containing up to 2.0 NCO/OH molar ratio; however, at 2.5, urethane and allophanate characteristic bands are present in both polymers. That reactivity is controlled by chemical kinetics since the activation barrier of the reaction between the GAP and TDI is 10 kcal.mol<sup>-1</sup> lower than in the corresponding reaction with the IPDI. This difference results from the sum of the higher hyperconjugative interactions, approximately 65%, and the lower steric hindrance, about 35%, in the activated complex containing the TDI.

**Keywords:** Allophanate; GAP; Hiperconjugative interaction; Steric hindrance.

## INTRODUCTION

The glycidyl azide polymer (GAP) has been reported as an energetic binder in the literature for at least 30 years (Ampleman 1993; Beaupré *et al.* 2003; Frankel *et al.* 1988; Keicher *et al.* 2009; Lee *et al.* 2019. Min *et al.* 2014). GAP is a prepolymer with a molar mass varying from 1,500 g.mol<sup>-1</sup> to 2,600 g.mol<sup>-1</sup> (Frankel *et al.* 1992) and presents terminal secondary hydroxyl reactive groups and azide groups, which confer energetic character to this material.

In order to achieve a solid material with mechanical resistance, GAP prepolymer should react with a chain extensor. A conventional reaction that allows the increase in GAP molar mass is through the reaction between GAP terminal secondary hydroxyl group and di or tri isocyanates (Hagen *et al.* 2015; Kasıkçı *et al.* 2001; Keskin and Özkaz 2001; Lee *et al.* 2019; Reshmi *et al.* 2015; Selim *et al.* 2000; Zhai *et al.* 2013), which is similar to that occurring among a polyol and diisocyanates, resulting in a polyurethane (PU).

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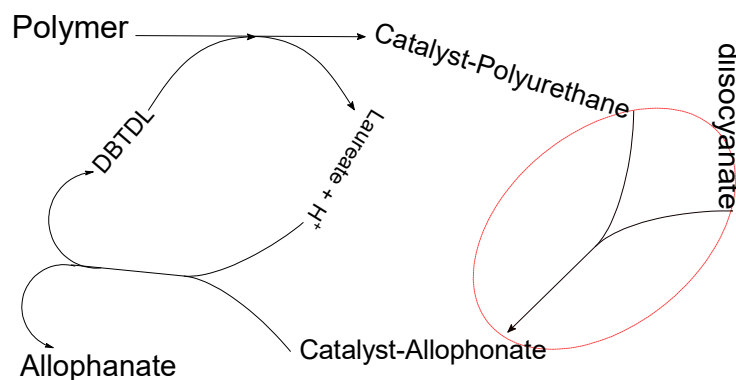


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The reaction between hydroxyl and isocyanate groups yields as a primary product a urethane group (Ionescu 2005; Szycher2012). Nonetheless, secondary reaction products have been reported in the literature. In particular, the formation of the allophanate group was described at NCO excess in the presence of a catalyst and temperatures around 50 °C (Ionescu 2005; Lapprand *et al.* 2005; Poljanšek *et al.* 2014; Reshmi *et al.* 2015; Sekkar *et al.* 2003). Lapprand *et al.* (2005) also cited the formation of heterocyclic isocyanurate in PU reactions at high NCO/OH ratios, elevated temperatures (~ 100 °C), and with a catalyst. The authors reported that the heterocyclic isocyanurate was the final product in these reaction conditions, while allophanate and urethane groups were detected only as intermediate reaction products.

Aromatic diisocyanates are more reactive than aliphatic ones due to the electron-withdrawing aryl group bonded to -NCO (Ionescu 2005). GAP polymer networking containing either toluene diisocyanate (TDI) or isophorane diisocyanate (IPDI) as curative agents has been reported in the literature (Eroglu and Guven 1998; Hagen *et al.* 2015; Manu *et al.* 2008, 2009; Min *et al.* 2014; Reshmi *et al.* 2015).

In the present study, polymers of GAP/TDI or GAP/IPDI were prepared using NCO/OH molar ratio varying from equimolar to NCO excess. Although energetic binders based on GAP and diisocyanates containing NCO excess do not yield propellant with adequate properties, this study aims to investigate the resulting polymer chemical structures and their dependence on NCO content and diisocyanate reactivity. An *in silico* experiment estimated the energies involved in the allophanate group formation in GAP/diisocyanate reactions at NCO excess. Sung *et al.* (2018) proposed that mechanisms for the reactions in which nucleophiles attack electrophilic centers as -NCO group have included steps like protonation/deprotonation, complex reactant-catalyst forming, regeneration of catalyst, and the formation of the N-C linkage (Fig. 1). In the present simulation, the focus was on evaluating the reactivity between urethane moieties from GAP/diisocyanate polymers and the -NCO functional group of aromatic (TDI) or aliphatic (IPDI) diisocyanate compounds, i.e., the N-C allophanate bond forming reaction step.



Source: Elaborated by the authors.

**Figure 1.** The proposed mechanism for the formation of allophanate compounds from PU and diisocyanate in excess NCO shows the investigated step highlighted by the dashed circle.

## MATERIALS AND METHODS

### GAP/diisocyanates polymers preparation

GAP was synthesized as described previously (Sciamarelli *et al.* 2009) and the hydroxyl content ( $0.93 \text{ mmol}\cdot\text{g}^{-1}$ ) was determined by potentiometric titration. GAP molar mass was monitored using a gel permeation chromatography (GPC) Waters 1515, with tetrahydrofuran (THF) ( $1 \text{ mL}\cdot\text{min}^{-1}$ ) at 40 °C as eluent. Three  $\mu$ -Styragel<sup>®</sup> columns (Waters HR 0.5, HR 1, HR 4) were used, with refractive index detector model 2414. The calibration was carried out with polybutadiene standards ( $M_n=57,700$ ,  $M_n=29,600$ ,  $M_n=13,300$ ,  $M_n=5,750$ ,  $M_n=2,860$ , and  $M_n=831$ ). The GAP average molar mass ( $M_w$ ) was  $1,534 \text{ g}\cdot\text{mol}^{-1}$ , and its polydispersity was 1.20.

TDI 80/20 from Pronor Petroquímica, IPDI, and dibutyl tin dilaurate (DBTDL) from Cesbra Chemistry were used as received. GAP/diisocyanate polymers were prepared with different NCO/OH molar ratios (1.0; 1.5; 2.0; and 2.5). The catalyst used, DBTDL, was added at 1/250 DBTDL/GAP weight ratio. Before the addition of diisocyanates, GAP was maintained under vacuum at 65 °C

for 12 hours to remove any traces of water. The GAP/diisocyanate mixtures were held under vacuum at 65 °C and 25 kPa for 7 days to allow a complete reaction between NCO and OH groups. The GAP polymers were named with the abbreviation of the monomers, GAP/TDI and GAP/IPDI, followed by the NCO/OH molar ratio, as shown in Table 1.

**Table 1.** GAP/diisocyanate polymers named according to NCO/OH molar ratio

NCO/OH molar ratio	Polymers	
1.0	GAP/TDI 1.0	GAP/IPDI 1.0
1.5	GAP/TDI 1.5	GAP/IPDI 1.5
2.0	GAP/TDI 2.0	GAP/IPDI 2.0
2.5	GAP/TDI 2.5	GAP/IPDI 2.5

Source: Elaborated by the authors.

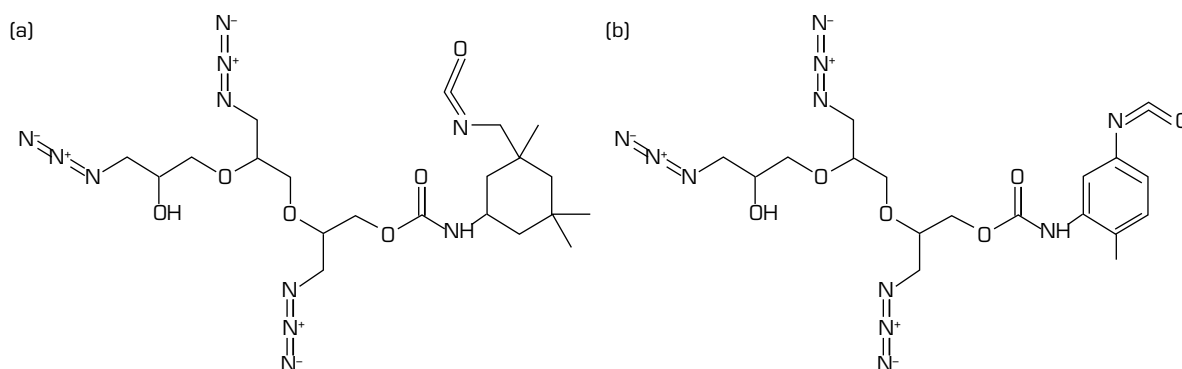
## Characterization

Glass transition temperature ( $T_g$ ) and GAP/TDI polymers were evaluated by differential scanning calorimetry (DSC Q100, TA Instruments) under nitrogen flow ( $50 \text{ mL}\cdot\text{min}^{-1}$ ) in a temperature range from  $-90$  to  $150$  °C at a heating rate of  $20$  °C $\cdot\text{min}^{-1}$ . The results reported in this study correspond to the second heating scan. The  $T_g$  was calculated at half height. The fraction of gel was evaluated by swelling test in THF solvent in accordance with the literature (Chung *et al.* 2012). GAP/TDI polymers (0.4-0.5 g) were immersed in THF for 24 hours. The polymers were then filtrated, evaporated, and weighed.

The FT-IR spectra were performed using a PerkinElmer Spectrum One spectrometer (resolution  $4 \text{ cm}^{-1}$ ; gain 1; 20 scans, MIR spectral range  $4000 \text{ cm}^{-1}$  to  $550 \text{ cm}^{-1}$  in the reflection mode with universal attenuated total reflection [UATR] accessory). The UATR accessory allows infrared spectra to be directly obtained from liquid samples (row materials) or solid samples (GAP polymers) with no additional sample preparation.

## In silico experiments

The unconstrained geometry optimizations have been carried out using the Firefly (Granovsky 2016; Schmidt *et al.* 1993) package at the HF/STO-3G(d,p) level (Frisch *et al.* 1984; Hehre *et al.* 1969; Pietro *et al.* 1981) with an algorithm based on the quadratic approximation (QA) (Jensen 1995) and a threshold gradient value of  $10^{-6}$  a.u. Frequency analyses were conducted to verify the nature of the obtained stationary structures. Intrinsic reaction coordinate (IRC) calculations were performed by the Gonzalez-Schlegel second-order method (Gonzalez and Schlegel 1991) with the former threshold gradient value and a step size between points on the reaction path of 0.2 a.u. The hyperconjugative and steric exchange interaction energies were calculated according to natural bond orbital (NBO) analyses (Glendening *et al.* 2004). Structures, charts, and surfaces were drawn by the wxMacMolPlt and Jmol software (Bode and Gordon 1998; Jmol 2004). The GAP/diisocyanate polymer models have three GAP monomers bonded to one diisocyanate compound (Fig. 2).



Source: Elaborated by the authors.

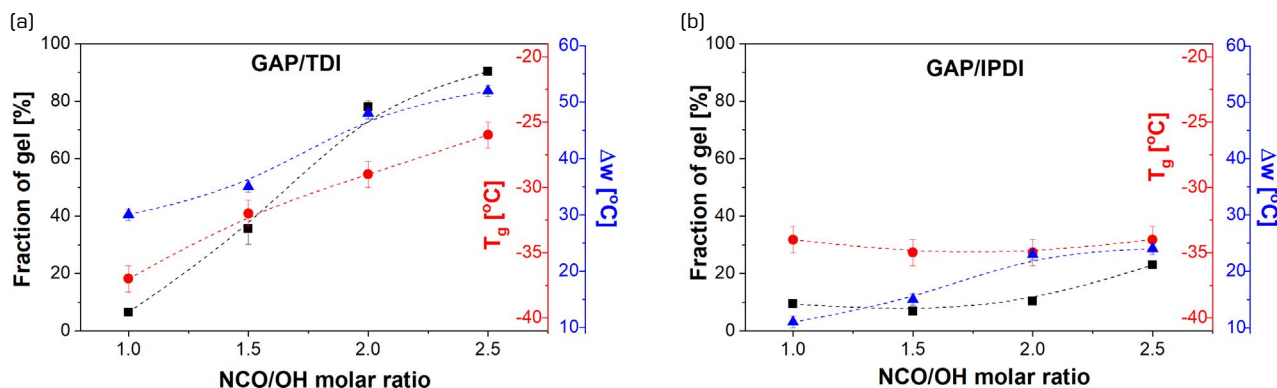
**Figure 2.** 2D oligomer structures used as polymeric model in computational studies: a) GAP/IPDI; b) GAP/TDI.

## RESULTS AND DISCUSSIONS

### Physical characterization

The GAP/TDI and GAP/IPDI polymers showed physical characteristics dependent on both NCO/OH molar ratio and diisocyanate nature, aliphatic, or aromatic. The appearance of the GAP/diisocyanate polymers changed from a solid paste at an NCO/OH equimolar ratio to a flexible solid at 2.5 NCO/OH molar ratio. Nonetheless, GAP/TDI 2.5 was similar to an elastomer, while the respective GAP/IPDI polymer presented yielding under tension as a thermoplastic. These characteristics indicated morphological differences between the polymers resulting from the addition of excess TDI or IPDI, suggesting the formation of a crosslinked molecular structure in the GAP/TDI polymers and linear chains as the predominant molecular structures in the GAP/IPDI polymers.

Crosslinking in the GAP/diisocyanate polymers was investigated by analyzing their gel fraction, estimated by performing swelling tests in THF. The variation of the gel fraction as a function of the NCO/OH molar ratio is shown in Fig. 3. At NCO/OH molar ratios greater than 1.0 for GAP/TDI polymers (Fig. 3a), the gel fraction displayed a substantial increase, reaching 90 wt% at NCO/OH 2.5. On the other hand, GAP/IPDI polymers (Fig. 3b) showed practically no change in the gel fraction from the equimolar ratio until NCO/OH 2.0, and at NCO/OH 2.5, the gel fraction was approximately 20 wt%.



Source: Elaborated by the authors.

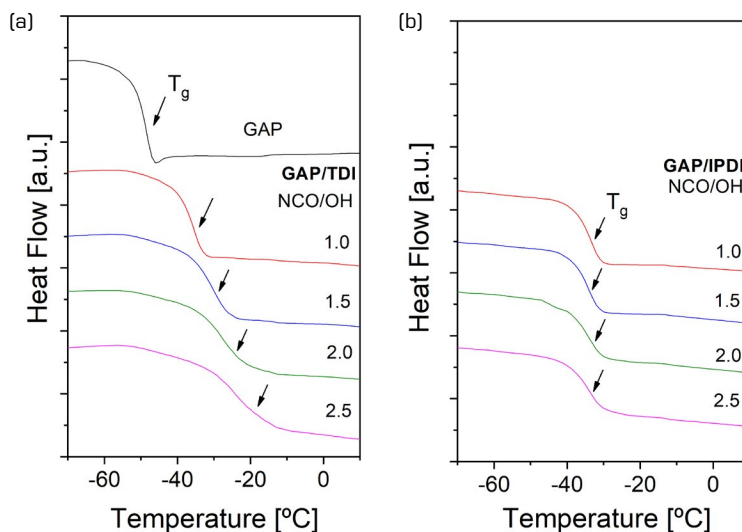
**Figure 3.** Physical properties of GAP/diisocyanate polymers: gel fraction [■];  $T_g$  [●];  $T_g$  width ( $\Delta w$ ) [▲].

The glass transition of polymers was investigated by DSC. These analyses were performed in two heating cycles in the same temperature range. The first heating scan was used to monitor an eventual residual reaction between GAP and diisocyanates due to the experimental conditions used in the preparation of the polymers. However, no exothermic peak was detected during the first heating scan, and the  $T_g$  obtained in the first and the second heating coincided. Both results indicated that all reactions occurred during the preparation of the polymers.

Sekkar *et al.* (2003) compared the influence of NCO/OH molar ratio in PU based on hydroxyl-terminated polybutadiene (HTPB) with TDI or IPDI, varying from 1 to 1.5. The authors reported that the crosslink density of HTPB/TDI with NCO/OH molar ratio 1.5 was approximately 1.5 superior to that found for the respective PU obtained with IPDI, and the  $T_g$  values of HTPB/diisocyanate PU did not change with the increase in NCO/OH molar ratio.

In the present study, the gel fraction observed for GAP/TDI containing NCO/OH molar ratios 1.5 and 2.5 were approximately 3.5 and 4.5 higher than those observed for the respective GAP/IPDI polymers. The high gel fraction observed for GAP/TDI polymers was a consequence of the higher reactivity of the aromatic diisocyanate as compared to the aliphatic one, like in the PU system studied by Sekkar *et al.* (2003). Another important difference between GAP/diisocyanate and HTPB/diisocyanate polymers is the reactivity of HTPB, which possesses primary hydroxyl groups. In contrast, GAP has secondary hydroxyl groups with lower reactivity, which can explain the low fraction of gel observed for the GAP/IPDI polymers, even in higher excess of diisocyanate groups compared to that reported in the literature (Sekkar *et al.* 2003) in HTPB/IPDI polymers.

GAP/diisocyanate polymers showed a single glass transition in DSC curves (Fig. 4), which indicates no phase segregation during the GAP and diisocyanates reaction, resulting in a predominant chemical structure related to each polymer composition. The GAP/TDI polymers presented a progressive increase in the  $T_g$  with the NCO/OH molar ratio increment (Fig. 3). This behavior follows the growth in the gel fraction, which agrees with a network formation in NCO excess in GAP/TDI polymers. The  $T_g$  increase as a function of the degree of crosslinking in PU was also reported by Sasaki *et al.* (1973). Additionally, in GAP/TDI polymers, a change in the glass transition profile was observed in DSC curves with the increment of the NCO/OH molar ratio, which resulted in a broadening of the glass transition region (Fig. 4a). This broadening is consistent with a network formation with different crosslink densities dependent on the NCO/OH molar ratio, analogous to the reported for thermosets (Chartoff *et al.* 2009).



Source: Elaborated by the authors.

**Figure 4.** DSC curves obtained for polymers with different NCO/OH molar ratios.

Manu *et al.* (2009) have studied GAP/TDI and GAP/IPDI polymers prepared in a mixture of 1,4-butanediol and 1,1,1-trimethylol propane as crosslinkers. They reported better mechanical properties for GAP/IPDI polymers, although the GAP/TDI polymer had a higher crosslink density. These authors attributed this behavior to the nature of the more homogeneous GAP/IPDI polymer containing mainly urethane linkages, which occurred because of the lesser extent of side reactions when compared with the more reactive aromatic diisocyanate. The authors also pointed out that many incomplete network linkages should be formed due to the side reactions in the GAP/TDI polymer.

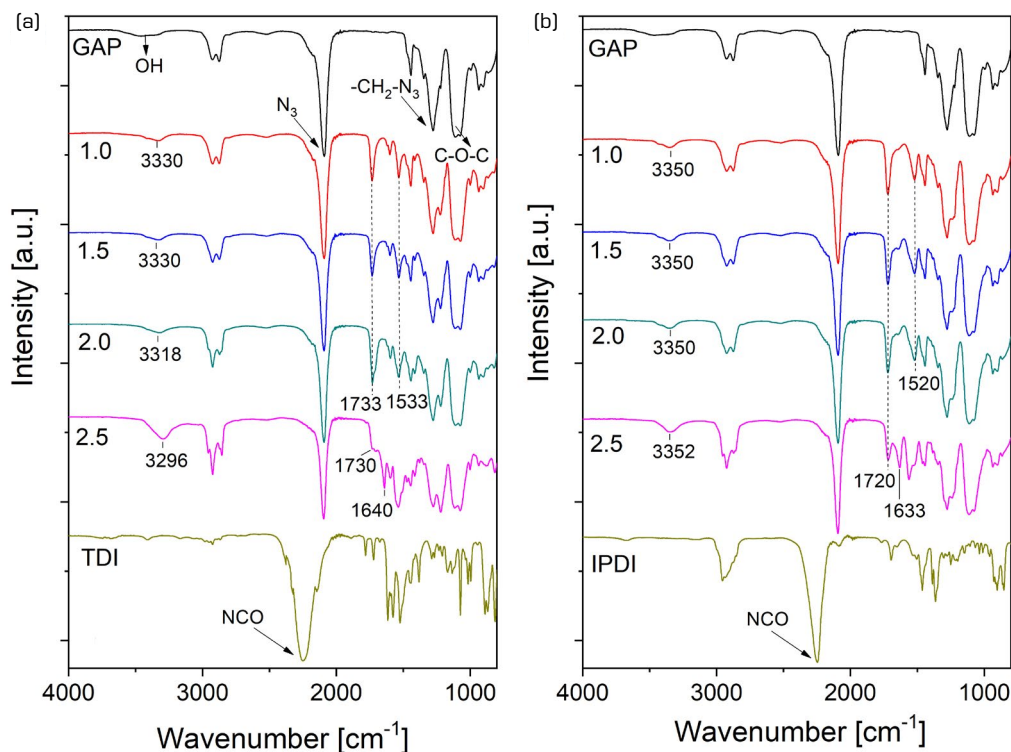
In the present study, NCO/OH equimolar GAP/IPDI polymer presented the narrowest glass transition width (Fig. 4b), along with the low fraction of gel comparatively to the other GAP/TDI polymers (Fig. 3), which agrees with the majority presence of urethane linkage in the equimolar ratio. The higher the NCO/OH molar ratio in GAP/TDI polymers, the broader the glass transition width, which indicates the formation of a heterogeneous network due to the side reactions and suggests a partially crosslinked network, as reported in the literature (Manu *et al.* 2009). Considering the experimental condition of the GAP polymer preparation, the network junction should mainly contain allophanate groups formed in NCO excess (Ionescu 2005; Lapprand *et al.* 2005; Szycher 2012).

### Infrared spectroscopy

Infrared spectroscopy of GAP/diisocyanate polymers was performed to verify the chemical changes at different NCO/OH molar ratios. In PU, secondary linkages can occur depending on the experimental conditions, including the catalyst addition, NCO/OH molar ratio, reaction temperature, and time. As previously mentioned, in the NCO excess, the presence of a catalyst, and moderate temperature (50-60 °C), the allophanate group formation is expected as a secondary reaction product along with the urethane group.

The FT-IR/UATR spectra (Fig. 5) show the GAP polymers, pure GAP, and the respective diisocyanate reactants. The main bands in the spectrum of pure GAP are observed at 2090  $\text{cm}^{-1}$  due to the stretching vibration of the  $\text{N}_3$  group and 1278  $\text{cm}^{-1}$  assigned to

$-\text{CH}_2-\text{N}_3$  absorption. The two bands at  $1110\text{ cm}^{-1}$  and  $1076\text{ cm}^{-1}$  are assigned to the ether group C-O-C vibration coupling (Frankel *et al.* 1992; Reshmi *et al.* 2015; Sciamareli *et al.* 2009; Wang *et al.* 2015). The GAP hydroxyl band is broadened, being observed between  $3600\text{ cm}^{-1}$  and  $3270\text{ cm}^{-1}$ . The main absorption in TDI (Fig. 5a) is observed at  $2250\text{ cm}^{-1}$ , assigned to the stretching of the -NCO group (Manu *et al.* 2009; Reshmi *et al.* 2015; Smith 1979), along with characteristic aromatic bands at  $1500\text{ cm}^{-1}$  and  $800\text{--}700\text{ cm}^{-1}$  (Smith 1979). The NCO band in IPDI is observed at  $2245\text{ cm}^{-1}$  (Fig. 5b).



Source: Elaborated by the authors.

**Figure 5.** FT-IR/UATR spectra of the GAP polymers (a) GAP/TDI and (b) GAP/IPDI.

The infrared spectra of GAP/diisocyanate polymers showed characteristic bands of the urethane groups for polymers obtained with NCO/OH molar ratio up to 2.0 (Fig. 5). In the literature, two absorptions have been reported in the carbonyl region for secondary urethane, one occurring between  $1715\text{--}1735\text{ cm}^{-1}$  ( $\nu_{\text{C=O}}$ ) and the other at  $1530\text{--}1540\text{ cm}^{-1}$  ( $\nu_{\text{C=O}}$ ) (Smith 1979). GAP/diisocyanate polymers containing up to 2.0 NCO/OH molar ratio showed carbonyl bands at  $1733\text{ cm}^{-1}$  and  $1533\text{ cm}^{-1}$  for GAP/TDI and bands at  $1720\text{ cm}^{-1}$  and  $1520\text{ cm}^{-1}$  for GAP/IPDI. In both GAP polymers, at 2.5 NCO/OH molar ratio, a spectral change occurred. However, in the GAP/TDI the spectral change was more pronounced, which can be attributed to the higher amount of allophanate group formed in this polymer. Koposov and Zharkov (1966) reported the splitting of the vibrations of the C=O group in allophanate, which were reported to occur at  $1736\text{ cm}^{-1}$  and  $1695\text{ cm}^{-1}$  in ethyl  $\alpha$ ,  $\gamma$ -diphenylallophanate. Furukawa and Yokoyama (1979) reported bands at  $1725\text{ cm}^{-1}$  and  $1693\text{ cm}^{-1}$  for C=O stretching for 1,3-diphenyl isopropyl allophanate. In GAP/diisocyanate polymers, only one new band in the region of the carbonyl group was observed at 2.5 NCO/OH molar ratio, occurring at  $1640\text{ cm}^{-1}$  and at  $1633\text{ cm}^{-1}$  for GAP/TDI and GAP/IPDI polymers, respectively, which may be due to the overlap of the urethane and allophanate bands. Beyond the changes in the carbonyl region observed for GAP/TDI polymers, the N-H band ( $\nu_{\text{N-H}}$ ) was progressively shifted for lower wave number, from  $3330\text{ cm}^{-1}$  to  $3296\text{ cm}^{-1}$ , suggesting that the higher the NCO content the higher the amount of hydrogen bonding present in this polymer (Fig. 5a). The hydrogen bonds are expected to involve the urethane -NH group as a proton donor and carbonyl or ether groups as hydrogen bond acceptors (Wolińska-Grabczyk *et al.* 2008). This result also points out the formation of an additional allophanate in GAP/TDI 2.5, which, along with urethane groups, may be responsible for the increase in the intensity of the -NH band.

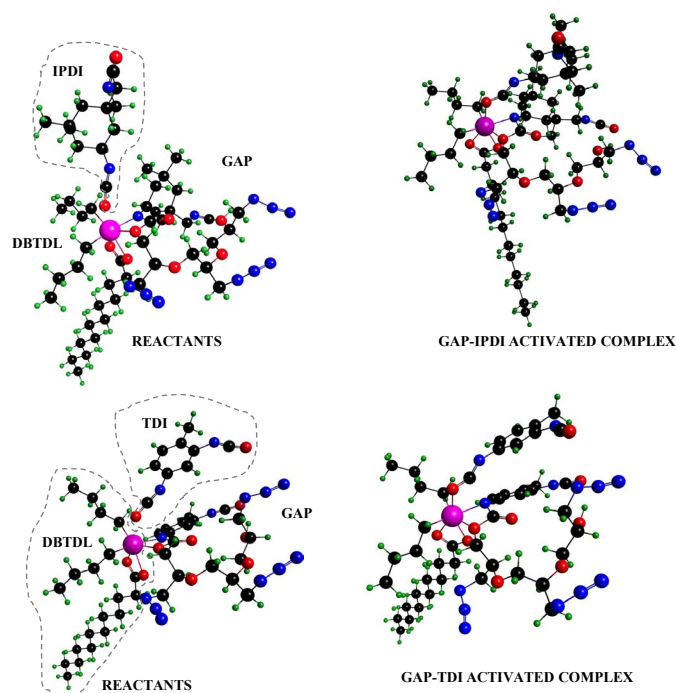
In GAP/IPDI polymers, the -NH band at  $3350\text{ cm}^{-1}$  practically was not shifted with the NCO/OH molar ratio variation (Fig. 5b). Moreover, the change in the intensity of the N-H band ( $\nu_{\text{N-H}}$ ) was lower in polymers containing IPDI than that observed for GAP/TDI. This behavior agrees with the lower gel fraction obtained for these polymers, attributed to the low allophanate amount formed in the presence of aliphatic diisocyanate.

### N-C allophanate quantum chemical simulations

In the present study, an *in silico* experiment was conducted considering the reaction energies between GAP polymers and diisocyanate excess. Minimum energy and transition states (TS) were identified, as shown in Fig. 6. The higher reactivity of the aromatic diisocyanate (TDI), as compared to the aliphatic one (IPDI), was attributed mainly to its kinetic stability since its transition structure showed a free energy of activation approximately  $10\text{ kcal.mol}^{-1}$  lower than that of the activated complex with an excess of the aliphatic diisocyanate (Table 2 and Fig. 7). This lower kinetic reaction energy of TDI allowed its excess to react with the PU in the presence of the DBTDL catalyst at  $60\text{ }^{\circ}\text{C}$ , resulting in the formation of allophanate groups. The origin of lower reaction barrier heights in the TDI-catalyst-polymer reaction system may be due to stronger hyperconjugative interactions and lesser steric effects in its activated complex compared to the IPDI-transition structure.

The total energy of hyperconjugative interactions (Fig. 8) between the lone pair of urethane nitrogen atom ( $n_{\text{Nurethane}}$ ) and unoccupied orbitals ( $n\rightarrow\pi^*$ ;  $n\rightarrow\sigma^*$ ) or lone pair of -NCO group ( $n\rightarrow n$ ) has accounted for nearly 65% of the energy difference of the activation barrier since they are about  $6\text{--}7\text{ kcal.mol}^{-1}$  more stable in the TDI-activated complex according to NBO analyses (Table 3). Additionally, the steric hindrance has destabilized the IPDI-transition structure by approximately  $3\text{--}4\text{ kcal.mol}^{-1}$  more than the respective TDI-activated complex (Table 4), corresponding to around 35% of the energy difference of the barrier content.

From the foregoing, hyperconjugative interactions and steric hindrance are major contributions to explaining the origin of the activation energies in reactions between GAP/diisocyanate polymers and excess of the diisocyanate, with the former making the main contribution to the reaction barrier height. Therefore, these *in silico* experiments agree with the experimental results, which indicated that the TDI excess may yield allophanate in a chemical reaction with GAP/TDI polymer catalyzed by DBTDL at  $60\text{ }^{\circ}\text{C}$ .



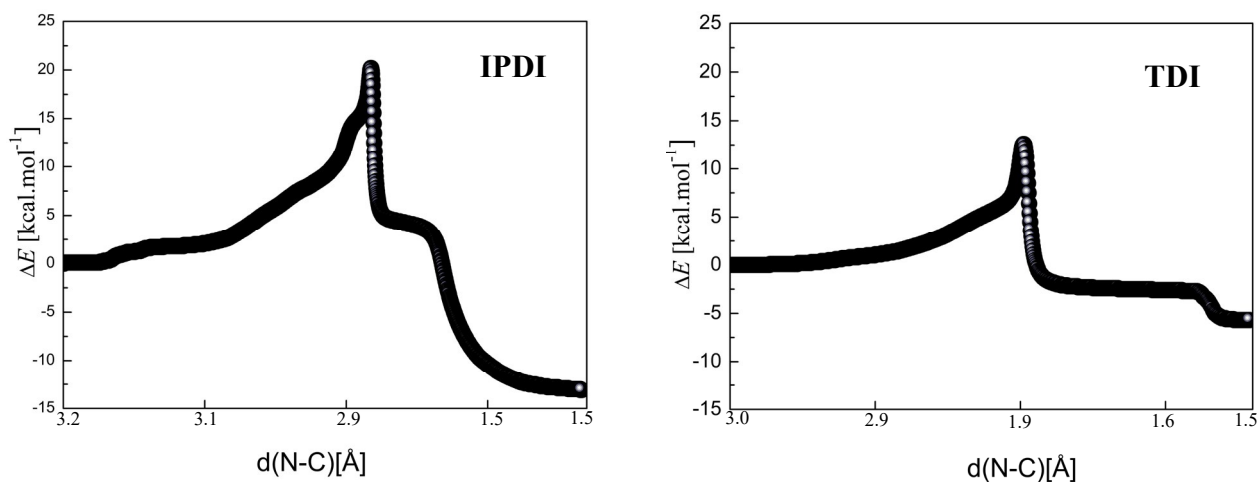
Source: Elaborated by the authors.

Figure 6. 3D structures of stationary states in the addition reactions of diisocyanate and urethane groups: carbon [●]; nitrogen [●]; oxygen [●]; hydrogen [●]; and tin [●].

**Table 2.** Activation parameters and interatomic distance in the rate-determining step investigated.

IPDI diisocyanate				
	$\Delta G^\ddagger(60\text{ }^\circ\text{C})^a$ [kcal.mol <sup>-1</sup> ]	$\Delta E_{\text{ZPE}}^\ddagger$ <sup>b</sup> [kcal.mol <sup>-1</sup> ]	$\Delta E^\ddagger$ <sup>c</sup> [kcal.mol <sup>-1</sup> ]	$d^d$ [Å]
Reactant	0.0	0.0	0.0	3.24
TS <sub>IPDI</sub>	20.2	20.3	23.6	2.06
TDI diisocyanate				
	$\Delta G^\ddagger(60\text{ }^\circ\text{C})^a$ [kcal.mol <sup>-1</sup> ]	$\Delta E_{\text{ZPE}}^\ddagger$ <sup>b</sup> [kcal.mol <sup>-1</sup> ]	$\Delta E^\ddagger$ <sup>c</sup> [kcal.mol <sup>-1</sup> ]	$d^d$ [Å]
Reactant	0.0	0.0	0.0	2.99
TS <sub>TDI</sub>	12.6	12.5	14.7	2.04

a:  $\Delta G^\ddagger$ (free energy of activation); b:  $\Delta E_{\text{ZPE}}^\ddagger$  (electronic + zero point energy of activation); c:  $\Delta E^\ddagger$  (electronic energy of activation); d:  $d$  (interatomic distance  $N_{\text{urethane}}-C_{\text{diisocyanate}}$ ). Source: Elaborated by the authors.



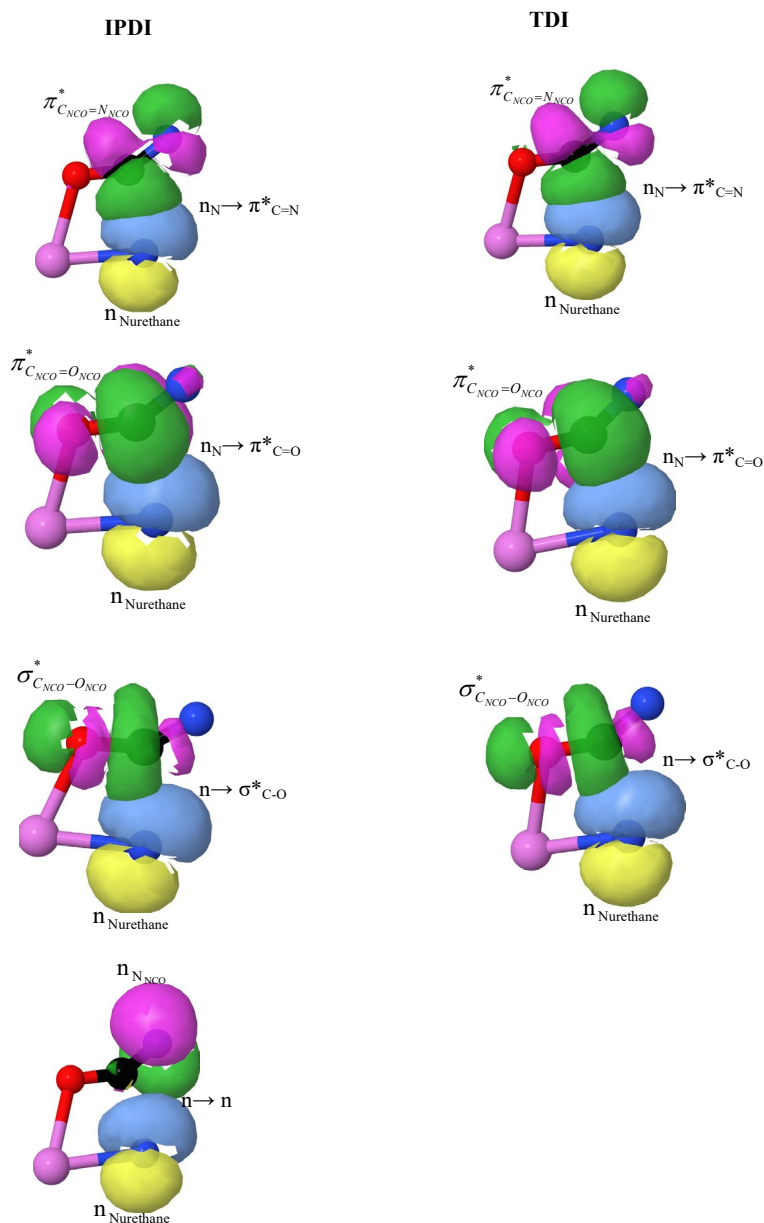
Source: Elaborated by the authors.

**Figure 7.** Energy versus bond length along the IRC for the allophanate group forming.**Table 3.** Relative NBO hyperconjugative interaction energies ( $\Delta E_{E2PRT}$ ) between NBO orbitals of activated complexes in the rate-determining step investigated.

Hyperconjugation	$\Delta E_{E2PRT}^a$ [kcal.mol <sup>-1</sup> ]
$n_{\text{Nurethane}} \rightarrow \pi^* C_{\text{NCO}} = N_{\text{NCO}}$	-9.5
$n_{\text{Nurethane}} \rightarrow \pi^* C_{\text{NCO}} = O_{\text{NCO}}$	0.8
$n_{\text{Nurethane}} \rightarrow \sigma^* C_{\text{NCO}} - N_{\text{NCO}}$	-0.1
$n_{\text{Nurethane}} \rightarrow N_{\text{NCO}}$	2.3
$\sum \Delta E_{E2PRT}^{(a)}$	-6.5

a:  $E_{\text{TS}_{\text{TDI}}} - E_{\text{TS}_{\text{IPDI}}}$ . Source: Elaborated by the authors.





Source: Elaborated by the authors.

**Figure 8.** Hyperconjugative interactions between electron densities of the urethanyl nitrogen atom and of the diisocyanate groups for the activated complexes in forming allophanate. Isosurface values = 0.03 a.u.; carbon [●]; nitrogen [●]; oxygen [●]; and tin [●].

**Table 4.** Relative NBO steric exchange energies [ $\Delta E_{\text{Steric}}$ ] between minimum and transition structures in the rate-determining step investigated.

	$\Delta E_{\text{Steric}}^a$ [kcal.mol <sup>-1</sup> ]
IPDI	45.0
TDI	41.3
$\Delta\Delta E_{\text{steric}}^b$	3.7

a:  $E_{\text{stericTS}} - E_{\text{steric reactant}}$ ; b:  $E_{\text{stericIPDI}} - E_{\text{stericTDI}}$ . Source: Elaborated by the authors.

## CONCLUSIONS

In the present study, the reactivity of isocyanate showed the greatest influence on the polymer molecular structure. The GAP reaction with an excess of the more reactive aromatic diisocyanate resulted in the crosslinked network, and its gel fraction increases as the NCO/OH molar ratio increases, achieving 90% at 2.5 NCO/OH molar ratio. Moreover, in GAP/TDI polymers, the  $T_g$  increased approximately 10 °C with the NCO/OH molar ratio increment. This crosslinked structure was attributed mainly to the allophanate group yielded by the reaction of the urethane group from GAP/TDI polymers and -NCO group from excess of TDI. On the other hand, GAP polymers with aliphatic diisocyanate presented thermoplastic characteristics for all compositions studied. Although the allophanate group was detected by FT-IR in GAP/IPDI 2.5, its concentration was lower than that observed for the respective GAP/TDI polymer, as verified by the low gel fraction, even with NCO excess. The studies *in silico* have corroborated the experimental results. The kinetic parameters explained the high reactivity of TDI since its activation barrier is more stable than IPDI in about 10 kcal.mol<sup>-1</sup>. Those molecular modeling simulations showed that the electronic structure of the TDI-activated complex has higher hyperconjugative interactions and lower steric hindrance than the IPDI-transition structure, corresponding to 65 and 35%, respectively, of the difference in barrier height for the reaction between GAP/diisocyanate polymers and NCO.


## AUTHOR'S CONTRIBUTION


**Conceptualization:** Dall'Agnol CB, Dutra RCL and Cassu SN; **Formal Analysis:** Dall'Agnol CB and Diniz MF; **Funding Acquisition:** Dutra RCL; **Investigation:** Dall'Agnol CB, Dutra RCL, Madureira LS and Cassu SN; **Methodology:** Dall'Agnol CB, Dutra RCL, Madureira LS and Cassu SN; **Project Administration:** Dall'Agnol CB, Dutra RCL and Cassu SN; **Software:** Madureira LS; **Supervision:** Dutra RCL and Cassu SN; **Visualization:** Dall'Agnol CB, Dutra RCL, Madureira LS and Cassu SN; **Writing – Original Draft Preparation:** Dall'Agnol CB, Dutra RCL, Madureira LS and Cassu SN; **Writing – Review & Editing:** Dutra RCL, Madureira LS and Cassu SN; **Final approval:** Cassu SN.

## DATA AVAILABILITY STATEMENT

Data will be available upon request.

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