

# Unexpected selectivity in the functionalization of neat castor oil under benign catalyst-free conditions

Latchmi C. Raghunanan\*, Inmaculada Martínez, Concepción Valencia, M. Carmen Sánchez, and José M. Franco\*

Pro2TecS-Chemical Product and Process Technology Research Centre. Departamento de Ingeniería Química, Facultad de Ciencias Experimentales, Universidad de Huelva, Campus de El Carmen, Huelva 21071, Spain.

\* franco@uhu.es; latchmi.singh@gmail.com

Supporting Information Placeholder

**ABSTRACT:** We present herein an unexpected selectivity in the reactions of castor oil with 1,6-hexamethylene diisocyanate (HMDI) in the absence of catalysts, heat or N<sub>2</sub> protection to give mono-functionalized castor oil derivatives. The reagents were stirred at room temperature for 24 hours, and the resulting formulations characterized with infrared spectroscopy, thermogravimetric analysis and NMR. In the highly viscous neat systems, the reaction stops at the formation of NCO-terminated urethane monomers. When the mass transfer limitations due to high viscosity are minimized, the NCO-terminated urethane monomers go on to form not di- or tri- urethane monomers, but crosslinked mono-urethane dimers. We propose that the selectivity of the functionalization reaction of castor oil originates from a hydrogen bonding mediated steric hindrance on two out of the three fatty acid moieties. This selectivity is normally associated with conformational preferences in crystallized triglycerides, and indicates an inherent level of structuring of the ricinolein molecules of neat castor oil. These findings indicate that unprecedented selective functionalization of triglycerides can be achieved under benign conditions, most notably without catalysts, representing a significant advancement for the production of more sustainable polymeric materials from renewable resources.

**KEYWORDS:** ricinoleic acid; urethane; pre-polymer; isocyanate; hydrogen bonding; liquid conformers.

## INTRODUCTION

Polyurethanes are among the most ubiquitous of polymers in present-day life; they are used to make materials with widely varying properties such as rigid and flexible foams, adhesives, coatings and plastic sheets.<sup>1</sup> In fact, polyurethanes are one of the most consumed classes of polymers after polyethylene, PVC, polystyrene and diene rubber.<sup>2</sup> Alcoholysis of isocyanates is the most employed method used industrially for the production of polyurethanes.<sup>2</sup> The reaction is typically dependent upon catalysts for high molecular weights,<sup>3</sup> but can be tuned to give widely different material properties simply by changing the nature of the reactants. For example, a polyurethane can be converted from an adhesive to a hard coating by increasing its crosslinking density (either via increasing the functionality of the alcohol or the con-

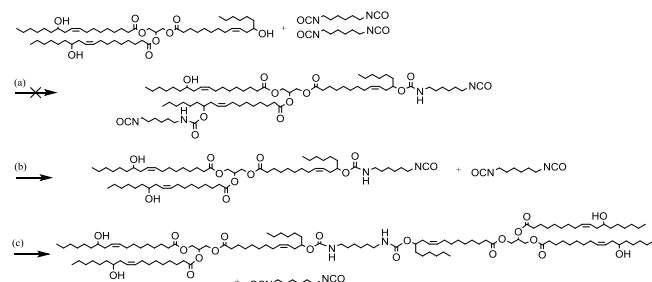
centration of isocyanate),<sup>4</sup> or from an elastomer to a foam by introducing water.<sup>5,6</sup>

In the absence of catalysts, the isocyanate undergoes nucleophilic attack by the hydroxyl group followed by proton transfer to the nitrogen moiety to give the urethane. This reaction is typically second order regardless of the chemical nature or source of the NCO and hydroxyl groups (Eqn. 1),<sup>2</sup> although the reaction rate constants themselves vary with the chemical reactivity of the reagents; primary alcohols and/or aromatic isocyanates react faster compared to secondary alcohols and/or aliphatic isocyanates.<sup>2,7</sup>

$$-d[\text{NCO}]/dt = k[\text{R-NCO}][\text{R}'\text{-OH}] \quad (1)$$

In this communication, we present the unexpected selectivity in the reaction of castor oil and hexamethylene diisocyanate (HMDI) to give mono-functionalized urethane prepolymers. As part of our ongoing work to understand the processing and curing kinetics of adhesives derived from renewably sourced raw materials, castor oil and HMDI were reacted in different amounts in order to obtain NCO-terminated prepolymers with varying degrees of functionalization. We expected that the degree of functionalization would increase with increasing NCO concentration during the processing stage (Scheme 1a), similar to what occurs during the curing stage.<sup>7</sup> Instead, however, we found that, regardless of the NCO starting concentration, the degree of castor oil functionalization was always the same (Scheme 1b-c).

**Scheme 1. Selective synthesis of NCO-terminated mono-urethane pre-polymer from castor oil and HMDI at room temperature.**



## MATERIALS & METHODS

Three concentrations of diisocyanate and castor oil were prepared; an equimolar HMDI:Castor oil ricinolein concentration such that total OH groups were in excess of NCO groups, and two concentrations having excess HMDI with respect to castor oil ricinolein (Table 1). Upon stirring at room temperature for 24 hours – in the absence of catalysts, heat and N<sub>2</sub> protection –, the resulting pre-polymers were immediately characterized by infrared (FTIR) and thermogravimetric analysis (TGA) experiments. Samples were also quenched by stirring in excess dry methanol and submitted to <sup>1</sup>H-NMR. More detailed information on the materials used and the procedures and methodologies followed to characterize the samples can be found in the Supporting Information.

## RESULTS & DISCUSSION

The results are presented in Figure 1; Figure 1a gives the FTIR spectra, Figures 1b and 1c show the TGA and corresponding DTG curves obtained from the thermal analysis experiments, and the

<sup>1</sup>H-NMR spectra are provided in Figure 1d. The assignment of the NMR peaks was supported by additional <sup>13</sup>C and 2D-NMR experiments (results in Supporting Information).

**Table 1. Nomenclature and chemical composition of reported urethane pre-polymers.**

Formulation nomenclature	8416	7525	6832
Weight ratio (castor oil: HMDI)	84:16	75:25	68:32
Mole ratio (ricinolein: HMDI)*	1:1.05	1:1.85	1:2.63
Mole ratio (OH:NCO)*	3:2.1	3:3.7	3:5.26
Isocyanate index (NCO:OH)	0.70	1.23	1.75

\*for simplicity, calculations assume that castor oil comprises 100% ricinolein.

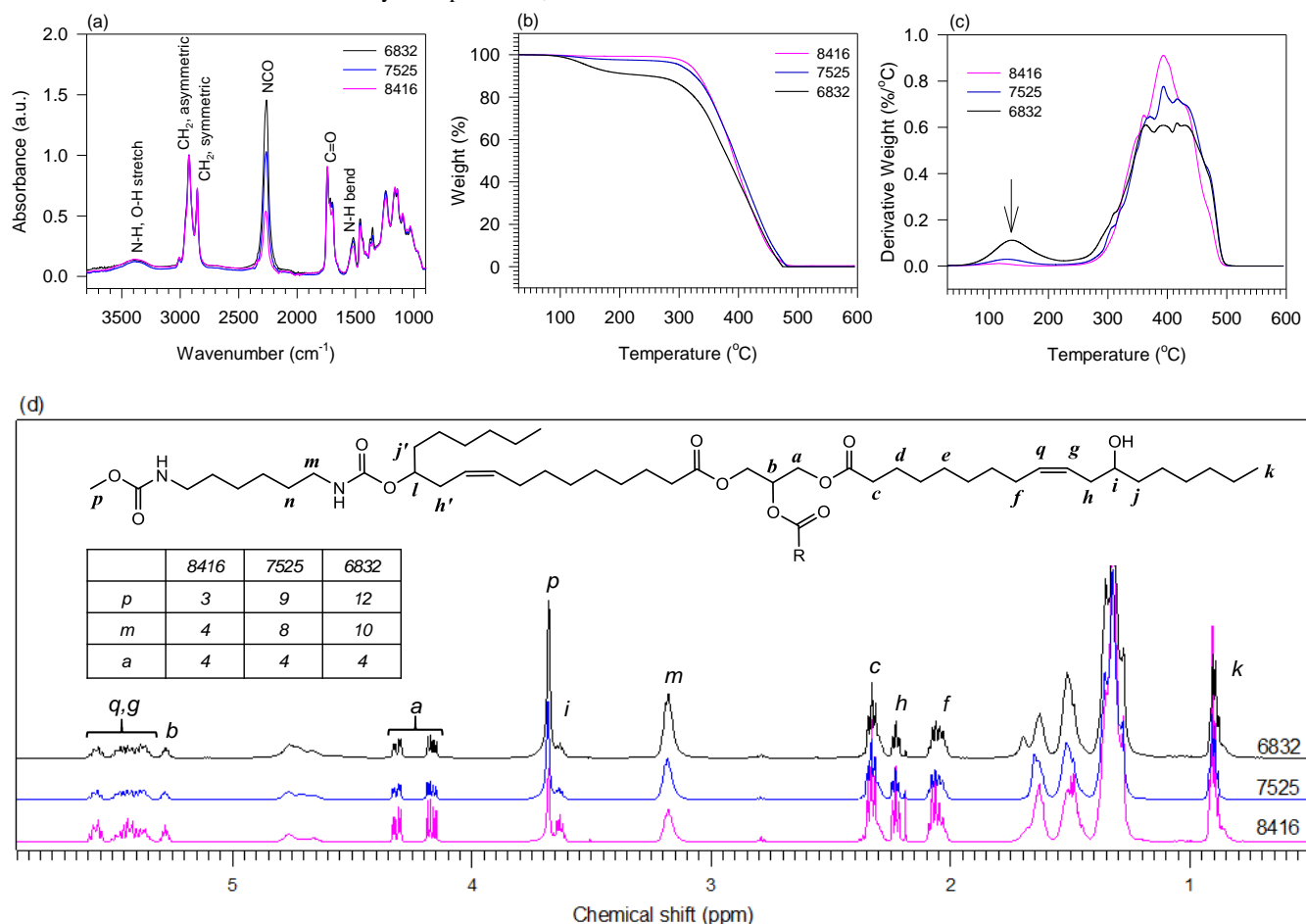


Figure 1. Chemical characterization of pre-polymers obtained from castor oil and HMDI following processing reaction. (a) FTIR spectra; (b) TGA curves and (c) Derivative TG (DTG) curves from TGA experiments; (d) <sup>1</sup>H-NMR spectra of methanol-quenched pre-polymers (Table inset in (d) lists integrals of the associated peaks, normalized to the glyceride CH<sub>2</sub> protons of a single triglyceride molecule).

From the FTIR spectra (Figure 1a), the formation of the urethane pre-polymers is confirmed by the presence of the amide II band (C-N stretching + N-H bending) at 1520 cm<sup>-1</sup> and the free and H-bonded C=O amide I stretching vibrations at 1715 and 1695 cm<sup>-1</sup>, respectively. The presence of unreacted isocyanates (NCO, 2266 cm<sup>-1</sup>) in all of the pre-polymer formulations is also apparent. Qualitative comparison of this peak in the different formulations

show that the number of unreacted isocyanates at the end of the processing stage increases with the isocyanate concentration.

From the TGA experiments (Figures 1b-c), a well-defined weight loss event between room temperature and ~ 250 °C, present in only the 7525 and 6832 formulations (arrow in Figure 1c), is attributed to the evaporation/boiling of free HMDI. The absence

of free HMDI in 8416 reveals that all of the unreacted NCO groups in the equimolar formulation are bound.

By quenching the pre-polymers with methanol, the proportion of urethanes formed during the processing stage compared to those formed upon quenching – and therefore the number of unreacted isocyanates just prior to quenching – can be deduced. In Figure 1d, the methyl carbamate group ( $\text{CH}_3\text{-O-(C=O)-NH-}$ ; 3H) – which is directly proportional to NCO quenched – occurs at 3.68 ppm, and the methylene group alpha to the urethane group ( $\text{CH}_2\text{-NH-(C=O)-O-}$ ; 4H) – formed by the reaction of the NCO with castor oil ricinolein and/or methanol – occurs at 3.18 ppm. The integral of each of these groups, normalized to a single triglyceride molecule, are tabulated in the inset of Figure 1d. Further normalization of these values to the number of protons per functional group (*i.e.*, 3 protons for O-CH<sub>3</sub> and 2 for CH<sub>2</sub>-NHCOO) gives the number of groups present per triglyceride molecule. The results (Supporting Information) show that the 8416, 7525 and 6832 formulations contain a total of 2, 4, and 5 urethane groups, respectively, of which 1, 3 and 4, respectively, are due to the urethanes produced upon the quenching of unreacted NCO groups. Therefore, in all of these formulations, each castor oil triglyceride molecule forms only one urethane bond with the HMDI; *i.e.*, regardless of NCO concentration, only a single fatty acid of each castor oil is functionalized during the processing stage (Scheme 1). This finding is further corroborated by additional <sup>13</sup>C and 2D NMR experiments performed on a representative unquenched sample (see Supporting Information).

Further inspection of the total urethanes per triglyceride in 6832, however, reveals that all of the pre-polymers are not NCO-terminated. For every 1 triglyceride molecule in 6832, only 5 urethane groups (*i.e.*, 2.5 molecules of HMDI) are accounted for; an NCO group on the third HMDI molecule is missing. Since all unreacted NCO groups must be converted into urethanes at the time of quenching, the hidden NCO must be bound to a second triglyceride molecule. Thus, in 6832 only, a single HMDI molecule is crosslinked between 2 castor oil molecules such that each triglyceride in castor oil still forms only one urethane bond with HMDI (Scheme 1c). It is likely that the dimerization reaction occurs in 6832 but not in 8416 and 7525 as a result of the large excess of HMDI in 6832 which act as a diluent to reduce the viscosity and, therefore, the mass transfer effects within the neat reaction system (see viscosity flow curves in the Supporting Information).

Surprisingly, these experimental results showed that castor oil is always mono-functionalized regardless of the NCO concentration; *i.e.*, only one fatty acid chain of each triglyceride is reactive during the processing stage – despite the excess availability of OH groups on castor oil and HMDI molecules in excess of castor oil. Since castor oil is predominantly composed of ricinolein (see Supporting Information), the difference in reactivities of the ricinoleic moieties must not originate from the nature of the fatty acid itself. The influence of steric barriers or mass transfer limitations preventing further functionalization of castor oil following the first reaction are also ruled out on account of the formation of dimers in 6832; if steric barriers alone were directing this reaction, we would have found castor oil di-urethane monomers (from the reaction of castor oil with the smaller more mobile HMDI molecules; Scheme 1a) instead of only the mono-urethane dimers (from reaction of the bulky castor oil and its urethane monomer; Scheme 1c).

This leaves only stereochemistry to account for the difference in reactivities of the ricinoleic acid moieties during the processing reaction. Typically, one does not expect conformational arrangement of triglycerides in the fluid state (Figure S4, Supporting

Information).<sup>8</sup> Precedence does exist, however, for such a scenario. Philippaerts *et al* have shown the existence of the tuning fork conformation in triglyceride solutions which resulted in the preferred reactivity of Pt/ZSM-5 zeolite with the double bonds at the *sn*-2 position of vegetable oils compared to the same fatty acids at *sn*-1 or *sn*-3.<sup>9</sup> Similar arguments may be extended for our systems, wherein the primary liquid state conformer has only one out of its three reactive fatty acid moieties sterically available. This will occur if the OH groups on the two remaining fatty acids are hydrogen bonded to other sterically bulky molecules – such as another ricinolein. In fact, the FTIR spectrum of castor oil (Supporting Information) shows two overlapping peaks at 3374 and 3523 cm<sup>-1</sup> which are associated with the hydrogen bonded and non-hydrogen bonded OH groups, respectively. Deconvolution of these peaks (Supporting Information) reveals that ~ 80% of the OH groups in ricinolein are hydrogen bonded; *i.e.*, only 20% are unencumbered and therefore available to participate in the functionalization reactions. This is a close approximation to the 33% functionalization deduced from the <sup>1</sup>H-NMR experiments. The differences in agreement are probably due to decreased hydrogen bonding density in neat castor oil upon addition of the HMDI reagent and/or constantly changing conformations associated with random motion in the fluid state. Moreover, analogous to the well-known shear-induced crystallization of vegetable oil triglycerides,<sup>10-11</sup> it is also probable that the conformational preferences observed for castor oil during the reaction occur as a result of shear-induced self-assembly of the ricinolein triglycerides – facilitated, of course, by hydrogen bonding of the OH groups on the ricinoleic acid moieties. We note further that since hydrogen bonding results in nucleophilic activation of the OH groups via polarization of the O-H bond<sup>12</sup> – analogous to what occurs in the base-catalyzed urethane synthesis<sup>3</sup> –, the energy barriers associated with the hydrogen bonded steric blocking must be greater. This is consistent with the known susceptibility of the base-catalyzed reaction to steric hindrance.<sup>13</sup>

In summary, we have unwittingly found that regardless of NCO concentration, a mono-functionalized castor oil urethane derivative is always formed during the processing stage of the uncatalyzed reaction. In the highly viscous systems of 8416 and 7525, this results in NCO-terminated urethane monomers. When the mass transfer limitations due to high viscosity is minimized, the NCO-terminated urethane monomers go on to form castor oil mono-urethane dimers. We propose that the selectivity towards the degree of functionalization in castor oil originates from hydrogen bonding mediated steric hindrance on two out of the three fatty acid moieties. Analogous stereo-selectivity is normally associated with conformational preferences in solid triglycerides, and indicates an inherent level of structuring of the ricinolein molecules of neat castor oil. These findings indicate that unprecedented selective functionalization of triglycerides can be achieved under benign conditions, most notably without catalysts, representing a significant advancement for the production of more sustainable materials from renewable resources. We acknowledge that further work is necessary to shed light on the mechanisms proposed; this, however, does not diminish from the significance and, more importantly, the implications, of the findings for existing and rapidly growing research areas such as lipid science and sustainable materials engineering. Suggested future work includes the use of computational models at the micro and macro scale levels to understand the intra- and inter- molecular interactions leading to the reported selectivity and conformational preferences of castor oil, as well as studies probing the role of shear on inducing conformational order within the neat system.

## ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Included in the Supporting Information: Detailed Materials & Methods, NMR spectra, viscosity flow curves, deconvolution of selected region of FTIR spectra.

## AUTHOR INFORMATION

### Corresponding Authors

\*J. M. Franco. E-mail: franco@uhu.es

\*L.C. Raghunanan. E-mail: latchmi.singh@gmail.com

### Present Address

L.C. Raghunanan: Trent Centre for Biomaterials Research, Departments of Physics & Astronomy and Chemistry, Trent University, 1600 West Bank Drive, Peterborough, ON, Canada K9L 0G2

### Notes

The authors declare no competing financial interests.

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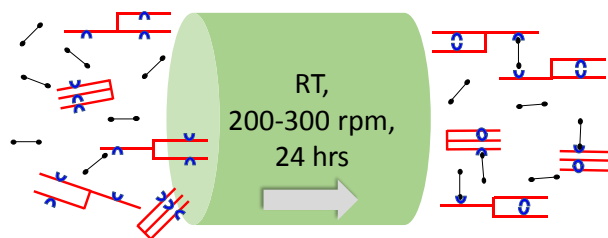
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**TOC:**



**Synopsis:**

We report the unprecedented selective functionalization of castor oil triglycerides - a significant advancement for the production of sustainable materials from renewable resources.