

Special Issue: Green and Sustainable Polyurethanes for Advanced Applications

Guest Editors: Prof. Sophie Guillaume (Universite de Rennes, France), Dr. Hamdy Khalil (Woodbridge Foam Corp., Canada), Prof. Manjusri Misra (University of Guelph, Canada)

EDITORIAL

Green and sustainable polyurethanes for advanced applications

Sophie Guillaume, Hamdy Khalil, Manjusri Misra, *J. Appl. Polym. Sci.* 2017, DOI: [10.1002/app.45646](https://doi.org/10.1002/app.45646)

RESEARCH ARTICLES

Polyurethanes prepared from cyclocarbonated broccoli seed oil (PUcc): New biobased organic matrices for incorporation of phosphorescent metal nanocluster

Patrick Loulergue, Maria Amela-Cortes, Stephane Cordier, Yann Molard, Loic Lemiegre, Jean-Luc Audic, *J. Appl. Polym. Sci.* 2017, DOI: [10.1002/app.45339](https://doi.org/10.1002/app.45339)

Non-isocyanate polyurethanes from six-membered cyclic carbonates: Catalysis and side reactions

Robert H. Lambeth, Sanyo M. Matthew, MyVan H. Baranoski, Kathleen J. Housman, Bao Tran, Jonathan M. Oyler, *J. Appl. Polym. Sci.* 2017, DOI: [10.1002/app.44941](https://doi.org/10.1002/app.44941)

Hydrogen bonds prevent obtaining high molar mass PHUs

Blain Marine, Adrien Cornille, Bernard Boutevin, Remi Auvergne, Dominique Benazet, Bruno Andrioletti, Sylvain Caillol, *J. Appl. Polym. Sci.* 2017, DOI: [10.1002/app.44958](https://doi.org/10.1002/app.44958)

Tuning the properties of segmented polyhydroxyurethanes via chain extender structure

Goliath Beniah, William H. Heath, Junho Jeon, John M. Torkelson, *J. Appl. Polym. Sci.* 2017, DOI: [10.1002/app.44942](https://doi.org/10.1002/app.44942)

Structural effects on the reprocessability and stress relaxation of cross-linked polyhydroxyurethanes

David J. Fortman, Jacob P. Brutman, Marc A Hillmyer, William R. Dichtel, *J. Appl. Polym. Sci.* 2017, DOI: [10.1002/app.44984](https://doi.org/10.1002/app.44984)

Non-isocyanate thermoplastic polyurethanes elastomers (NIPUs) based on PEG through the transurethanization approach

Nasreddine Kebir, Soumaya Nouigues, Pierre Moranne, Fabrice Burel, *J. Appl. Polym. Sci.* 2017, DOI: [10.1002/app.44991](https://doi.org/10.1002/app.44991)

Bio-based flexible polyurethane foams derived from succinic polyol: Mechanical and acoustic performances

Maria Oliviero, Ietizio Verdolotti, Mariamelia Stanzione, Marino Lavorgna, Salvatore Iannace, Maurizio Tarello, Andrea Sorrentino, *J. Appl. Polym. Sci.* 2017, DOI: [10.1002/app.45113](https://doi.org/10.1002/app.45113)

Impact of hard segment concentration on highly resilient polyurethane foams based on palm olein polyol

Srihanum Adnan, Maznee T. I. Tuan Noor, Nurul H. Ain, Kosheela P. P. Devi, Norhisham S. Mohd, Yeong Shoot Kian, Zainab B. Idris, Irma Campara., Christi M. Schiffman, Karol Pietrzyk, Vahid Sendijarevic, Ibrahim Sendijarevic, *J. Appl. Polym. Sci.* 2017, DOI: [10.1002/app.45440](https://doi.org/10.1002/app.45440)

Antimicrobial polyurethane foams having cationic ammonium groups

Esther Udabe, Mehmet Isik, Haritz Sardon, David Mecerreyes, Lourdes Irusta, Maitane Salsamendi, Feng Yan, *J. Appl. Polym. Sci.* 2017, DOI: [10.1002/app.45473](https://doi.org/10.1002/app.45473)

Polyurethane/esterified cellulose nanocrystal composites as a transparent moisture barrier coating for encapsulation of dye sensitized solar cells

Kitti Yuwawech, Jatuphorn Wootthikanokkhan, Sompit Wanwong, Supachok Tanpichai, *J. Appl. Polym. Sci.* 2017, DOI: [10.1002/app.45010](https://doi.org/10.1002/app.45010)

Hydrophobic-hydrophilic surface switching properties of non-chain extended poly(urethane)s for use in agriculture to minimize soil water evaporation and permit water infiltration

Priscilla Johnston, George Freischmidt, Christopher D. Easton, Mark Greaves, Phillip S. Casey, Keith L. Bristow, Pathiraja A Gunatillake, Raju Adhikari, *J. Appl. Polym. Sci.* 2017, DOI: [10.1002/app.44756](https://doi.org/10.1002/app.44756)

Preparation, characterization and in vitro evaluation of chicken feather fiber/thermoplastic polyurethane composites

Özge Gökce, Murat Kasap, Gürler Akpınar, Güralp Özkoc, *J. Appl. Polym. Sci.* 2017, DOI: [10.1002/app.45338](https://doi.org/10.1002/app.45338)



Nonisocyanate thermoplastic polyurethane elastomers based on poly(ethylene glycol) prepared through the transurethanization approach

Nasreddine Kébir, Soumaya Nouigues, Pierre Moranne, Fabrice Burel

Unités Mixtes de Recherche (Centre National de la Recherche Scientifique) 6270 and FR 3038, Laboratoire Polymères Biopolymères Surfaces, Institut National des Sciences Appliquées de Rouen, Normandie Université, Avenue de l'Université, 76801 Saint Etienne du Rouvray, France

Correspondence to: N. Kébir (E-mail: nasreddine.kebir@insa-rouen.fr)

ABSTRACT: Nonisocyanate thermoplastic polyurethane elastomers (NIPUs) were synthesized with the transurethanization approach. Dimethyl dicarbamates (DCs) were prepared by the reaction of a diamine with an excess of dimethyl carbonate in the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a catalyst. Then, the polymers were obtained under neat conditions through the reaction of DC with polyethyleneglycol of average molecular weight of 1500 g/mol (PEG1500) at variable temperatures in the presence of different amounts of 1,4-butanediol. TBD, dibutyltin dilaurate (DBTL), and K_2CO_3 were tested as catalysts. TBD and DBTL seemed to be more efficient than K_2CO_3 in the temperature range 140–160 °C. The obtained materials exhibited molecular weight values (M_w) up to 10,000 g/mol and thermal stabilities above 200 °C. The soft segments displayed glass-transition temperature values that varied from –49 to –1 °C and melting temperature values that varied from 38 to 49 °C. Compared to polyurethane analogs, the NIPUs exhibited higher crystallinities and thermal stabilities. © 2017 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2017**, *134*, 44991.

KEYWORDS: elastomers; polycondensation; polyurethane; thermoplastics; thermal properties

Received 5 December 2016; accepted 13 February 2017

DOI: 10.1002/app.44991

INTRODUCTION

Polyurethanes (PUs) belong to the most important polymer families. They have versatile properties and are applied in several fields, including automotives, shipbuilding, footwear, medical devices (e.g., heart valves, artificial veins, cardiovascular catheters), and the controlled release of drugs and therapeutics.

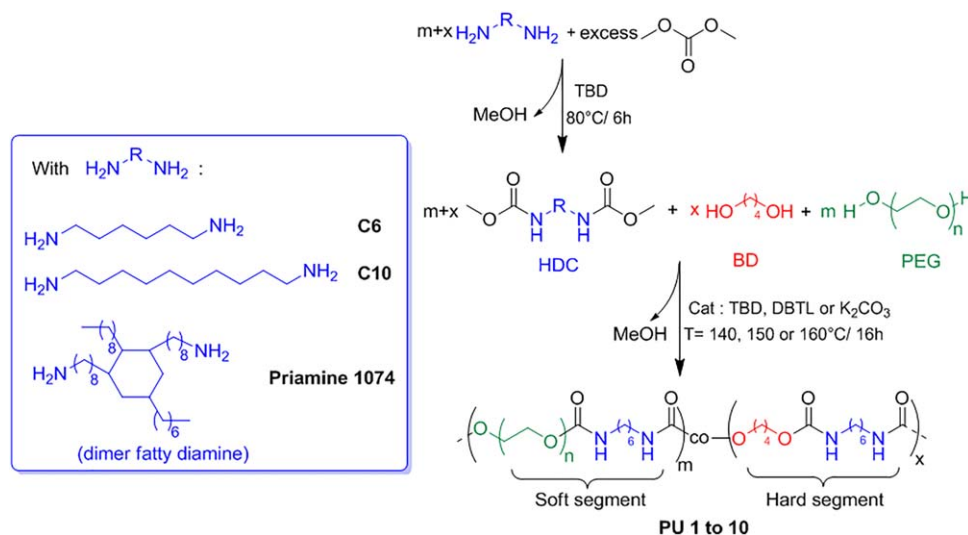
PUs are typically prepared by the reaction of monomers bearing isocyanate and hydroxyl functionalities. PU elastomers are obtained by the reaction of a flexible macrodiol (or polyol), called the *soft segment*, with a stiff part based on a diisocyanate and a chain extender, called the *hard segment*. Poly(ethylene glycol) (PEG) is either introduced as a comonomer in the soft part of PU materials or grafted on the surface. Thus, PUs based on PEG can be used in several application fields, including biomaterials^{1–7} and biodegradable,⁸ waterborne,⁹ water-soluble,¹⁰ thermoresponsive,¹¹ and energy-storage¹² materials. For biomedical applications, PEG has many advantages; it has a high resistance to protein adsorption and is antifouling, nontoxic, biocompatible, nonimmunogenic, nonantigenic, and soluble in various solvents, including water. Nevertheless, PEG is not biodegradable

but can easily be eliminated from the body by the renal system.¹³

For instance, Divakaran *et al.*¹ described porous PEG–PU hydrogels as potential biomaterials. They used PEG4000 as a soft segment, 4,4'-methylene biscyclohexylisocyanate as a hard segment, and 1,2,6-hexanetriol as a crosslinking agent. Cipolatti *et al.*² reported the synthesis of PU from PEG (PEG400, PEG4000, and PEG6000), polycaprolactone diol, and isophorone diisocyanates through a miniemulsion polymerization technique to produce a support for enzyme immobilization and stabilization. Park *et al.*³ prepared a functionalizable, reverse thermal gel based on a PU–PEG block copolymer as a potential biomaterial for tissue engineering and drug delivery. Mo *et al.*⁴ described a series of shape-memory PUs for biomedical applications synthesized by the bulk polymerization method from liquefied 4,4'-diphenyl methane diisocyanate, 1,4-butanediol (BD), and PEG (PEG6000). Ikeda *et al.*⁵ prepared blood-compatible segmented PUs and poly(urethane–urea)s from an ABA-type triblock copolyether as a prepolymer, where A was poly(ethylene oxide) and B was poly(tetramethylene oxide). These polymers

Additional Supporting Information may be found in the online version of this article.

© 2017 Wiley Periodicals, Inc.



Scheme 1. Synthesis of thermoplastic NIPU elastomers from DMC, diamines, BD, and PEG1500. Cat = catalyst; T = temperature. [Color figure can be viewed at wileyonlinelibrary.com]

were evaluated as drug-delivery matrixes, with crystal violet and benzethonium chloride as model drugs.

Nowadays, the development of sustainable, alternative, and environmentally friendly routes to PUs through nonisocyanate and nonphosgene pathways is of great interest.^{14–17} During the last decades, three main approaches have been developed:

1. The aminolysis of five-membered bicyclocarbonates by diamines to afford poly(hydroxyl urethane)s.^{17–27}
2. The self-polycondensation of AB-type fatty monomers containing hydroxyl and acyl azide groups, in the presence or absence of catalyst. The heating of acyl azide groups causes the *in situ* formation of isocyanate groups via Curtius rearrangement.^{28–30}
3. Transurethane polycondensation,^{31–43} particularly the one with the reaction between dimethyl dicarbamates (DCs) and diols in the presence of a catalyst, namely, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD).^{31–33}

In this article, we describe a process that allowed us to prepare nonisocyanate thermoplastic polyurethane elastomers (NIPUs) through the transurethane polycondensation with DCs as isocyanate substitutes. An original combination of dimethyl carbamate, BD as a chain extender, PEG1500 as a polyol, and TBD as an organocatalyst, was used. The reaction was conducted at several temperatures (<170°C). Other catalysts were tested, including K₂CO₃ and dibutyltin dilaurate (DBTL), which was used for the first time for this kind of reaction (Scheme 1). The process conditions were optimized. The physical properties of the obtained materials were assessed and compared to those of a polymer analog made from isocyanates.

EXPERIMENTAL

Materials

Dimethyl carbonate (DMC; 99%, anhydrous), BD (>99%), 1,6-diaminohexane (98%), DBTL, PEG [number-average molecular

weight (M_n) = 1500 g/mol from supplier], hexamethylene diisocyanate (HDI; ≥ 99%), and TBD (98%) were purchased from Sigma-Aldrich. Potassium carbonate (anhydrous) was obtained from VWR Prolabo. 1,10-Diaminodecane (97%) was purchased from TCI. The dimer fatty diamine (trade name Priamine 1074) was obtained from CRODA. All of the solvents and the other reagents were used as received.

Synthesis

General Procedure for Preparing DC from Diamine. In a 250-mL flask, 10 equiv of DMC, 0.1 equiv of TBD, and 1 equiv of diamine were added and stirred for 6 h at 80°C. Then, the medium was cooled to room temperature. Crystallized products were recovered by filtration (yield > 90%). In the case of Priamine 1074, the product was washed with water in a diethyl ether medium to remove TBD (yield ≈ 90%).

Dimethylhexane-1,6-Dicarbamate (HDC). ¹H-NMR (300 MHz, CDCl₃, δ): 4.67 (s, broad, 2H; NH), 3.65 [s, 6H; NH(CO)OCH₃], 3.15 (m, 4H; NHCH₂); 1.48 (m, 4H; NHCH₂CH₂), 1.32 (m, 4H; NHCH₂CH₂CH₂). ¹³C-NMR (75 MHz, CDCl₃, δ): 157.1 (C=O), 52.0 (CH₃), 40.7 (CH₂), 29.9 (CH₂), 26.2 (CH₂). IR [attenuated total reflection (ATR), ν, cm⁻¹]: ~3300 [m; ν_{NH}(carbamate)], ~1700 [s, ν_{CO}(carbamate)].

From differential scanning calorimetry (DSC), we obtained a melting temperature (T_m) of 98°C and a melting enthalpy (ΔH_m) of 111 J/g. From thermogravimetric analysis (TGA), we obtained a degradation temperature at 5% weight loss ($T_{5\%}$) of 152°C and a maximum degradation temperature (T_{max}) of 222°C.

Dimethyl 1,10-Decylenedicarbamate. ¹H-NMR (300 MHz, CDCl₃, δ): 4.68 (s, broad, 2H; NH), 3.67 [s, 6H; NH(CO)OCH₃], 3.17 (m, 4H; NHCH₂), 1.49 (m, 4H; NHCH₂CH₂), 1.29 (m, 12H; NHCH₂CH₂CH₂CH₂CH₂). ¹³C-NMR (75 MHz, CDCl₃, δ): 157.1 (C=O), 52.0 (CH₃), 40.9 (CH₂), 30.0 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 26.7 (CH₂). IR

(ATR, ν , cm^{-1}): ~ 3300 [m; $\nu_{\text{NH}}(\text{carbamate})$], ~ 1700 [s, $\nu_{\text{CO}}(\text{carbamate})$].

From DSC, we obtained a T_m of 111°C and a ΔH_m of 166 J/g . From TGA, we obtained a $T_{5\%}$ of 195°C and a T_{max} of 257°C .

DC of Priamine 1074. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 4.68 (s, broad, 2H; NH), 3.65 [s, 6H; $\text{NH}(\text{CO})\text{OCH}_3$], 3.15 (m, 4H; NHCH_2), 1–2 (m, 60H; CH and CH_2), 0.88 (m, 6H; CH_3). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , δ): 157.0 (C—O), 51.9 (CH_3), 41.0 (CH_2), 30.0 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.7 (CH_2), 22.7 (CH_2), 14.1 (CH_3). IR (ATR, ν , cm^{-1}): ~ 3300 [m; $\nu_{\text{NH}}(\text{carbamate})$], ~ 1700 [s, $\nu_{\text{CO}}(\text{carbamate})$].

From DSC, we obtained a T_m of less than -80°C . From TGA, we obtained a $T_{5\%}$ of 258°C and a T_{max} of 331°C .

General Procedure for the Synthesis of Nonisocyanate PUs (PU1–PU6). In a round-bottomed Schlenk flask equipped with a magnetic stirrer and a nitrogen inlet, HDC, PEG1500, BD, and a catalyst were added at a molar ratio of $1 + x:1:x:0.1$, respectively. The temperature was progressively increased to 140, 150, or 160°C under nitrogen flow and stirring. Then, the polymerization reaction was conducted over 16 h. Finally, after it was cooled to room temperature, the obtained PU was solubilized in dichloromethane, precipitated in petroleum ether, and then analyzed by $^1\text{H-NMR}$, Fourier transform infrared (FTIR) spectroscopy, size exclusion chromatography (SEC), DSC, and TGA.

Procedure for the Synthesis of PU (PEG–HDI). In a round-bottomed Schlenk flask equipped with a magnetic stirrer and a nitrogen inlet, HDI, PEG1500, and DBTL were added at a molar ratio of 1:1:0.1. The temperature was progressively increased to 80°C under nitrogen flow and stirring. Then, the polymerization reaction was conducted over 2 h. Finally, after it was cooled to room temperature, the obtained PU was solubilized in dichloromethane, precipitated in petroleum ether, and then analyzed by $^1\text{H-NMR}$, FTIR spectroscopy, SEC, DSC, and TGA.

Measurements and Instrumentation

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Bruker 300 Fourier transform spectrometer at 300 and 75 MHz, respectively, in CDCl_3 solutions with tetramethylsilane as an internal standard.

The IR spectra were recorded on an FTIR spectrometer (PerkinElmer Spectrum 2000 FTIR) equipped with a diamond ATR device. Spectra were obtained from 10 scans in the 4000 – 500-cm^{-1} range.

The polymer average molecular weights [M_n and weight-average molecular weight (M_w)] and dispersity (M_w/M_n) were determined by SEC. The polymers were dissolved in CH_2Cl_2 , filtered ($0.45\text{ }\mu\text{m}$), and analyzed at 25°C with a Varian PL-GPC50 device equipped with two mixed packed columns (PL gel mixed, type C). The mobile phase was CH_2Cl_2 and poly(methyl methacrylate) (PMMA) standards (from 875 to $680,000\text{ g/mol}$) were used for calibration.

TGA measurements were performed on a TGA Q500 system (TA Instruments) under a nitrogen atmosphere at a heating rate of 10°C/min to determine $T_{5\%}$ and T_{max} .

DSC was performed on a DSC Q2000 apparatus (TA Instruments) under nitrogen at a heating rate of 10°C/min . The glass-transition temperature (T_g) was measured at the midpoint. T_m was determined at the maximum of the endothermic peak. Thermograms were recorded in the temperature range of -80 to 200°C .

RESULTS AND DISCUSSION

Monomer Preparation and Characterization

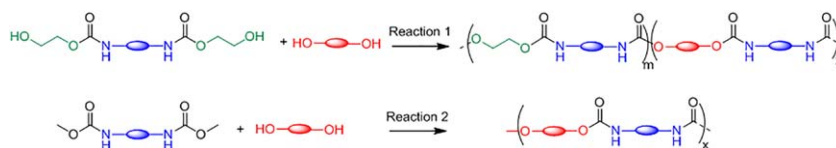
We started this study with the synthesis of DC monomers by the reaction of a selected diamine with DMC in the presence of TBD as a catalyst (Scheme 1) and according to a method described elsewhere.^{31,33} These monomers are of great interest because they can be biosourced, versatile, and substitutes for diisocyanate agents for the synthesis of classical PUs. DMC is a green solvent and is an ideal substitute for phosgene. It can be prepared from carbon dioxide and methanol (MeOH)⁴⁴ or from urea and MeOH ⁴⁵ as renewable materials. In addition, it can be infinitely recycled by simple distillation. 1,6-Hexanediamine, 1,10-decanediamine, and Priamine 1074 were selected as biosourced diamines. 1,6-Hexanediamine can be synthesized from glucose or starch.^{46–48} 1,10-Decanediamine is obtained from castor oil.⁴⁶ Priamine 1074 is prepared from linoleic and/or oleic acid and displays a branched and saturated cycloadduct structure (molecular weight (M) = 534 g/mol). These diamines were reacted with a large excess of DMC to prevent chain extension. The reaction was conducted at 80°C for 6 h. In previous studies,^{31,33} the purification of these dicarbamates was conducted by flash-column chromatography, which is not suitable or desirable for the industrial scale. In this study, linear DCs were recovered in high yields by crystallization at room temperature. The branched DC of Priamine 1074 was extracted in organic medium after washing with water.

$^1\text{H-NMR}$ analysis of the DCs revealed a total conversion of the amine groups through the absence of the signal of CH_2 protons in the α position to these groups around 2.68 ppm. Methyl protons of the methyl carbamate groups displayed a signal at 3.65 ppm, whereas the methylene groups in the α position to this function arose around 3.15 ppm. The nitrogen proton signal was also observed around 4.68 ppm. Moreover, the FTIR bands corresponding to the vibration of C—O bonds ($\sim 1700\text{ cm}^{-1}$) and to the vibration of N—H bonds ($\sim 3300\text{ cm}^{-1}$) of the methyl carbamate group were clear. HDC and dimethyl 1,10-decylenedicarbamate exhibited T_m s of 98 and 111°C , respectively. The DC of Priamine 1074 did not display a T_m . TGA revealed the good thermal stability of these monomers, that is, with a $T_{5\%}$ from 152 to 258°C and a T_{max} from 222 to 331°C ; this was similar to our previous results.^{31,33}

Preparation and Characterizations of NIPUs

Transurethane polycondensation is a promising pathway for the preparation of thermoplastic NIPUs. Overall, two kinds of reactions can be distinguished:

1. The reaction of diols with dihydroxyethyl dicarbamates, which is the oldest one.^{34–39} This reaction involves stannous catalysts, a high temperature ($\geq 170^\circ\text{C}$), and a high vacuum to eliminate the ethylene glycol formed during



Scheme 2. Two reactions related to transurethane polycondensation. [Color figure can be viewed at wileyonlinelibrary.com]

polycondensation. In addition, under these conditions, dihydroxyethyl dicarbamates exhibit self-polycondensation, and this leads to the formation of hard segments with uncontrolled length. In addition, urea linkages can be formed because of a back-biting side reaction.³⁸

2. The reaction of diols with DCs, especially when TBD is used as organic catalyst at 160 °C.^{31–33} In this case, nitrogen flow was sufficient to eliminate the released MeOH and displace the equilibrium toward polymer's formation. MeOH can be recovered by condensation with, for instance, a cold trap (water or carbonic ices). Furthermore, neither the self-polymerization of DCs nor back-biting side reactions are observed. However, when $\text{Ti}(\text{OBu})_4$ ^{40,41} or dibutyltin oxide^{42,43} are used as catalysts, the reaction needs a high temperature and a vacuum to occur. Thus, the polymers synthesized from reactions 1 and 2 could not have the same chemical structures (Scheme 2).

Recently, with reaction 1, Li *et al.*³⁵ prepared amorphous cycloaliphatic thermoplastic NIPU elastomers by reacting di(hydroxyethyl)isophorone biscarbamate with different PEGs (400, 600, 1000, 1500, 2000, and 4000). Thus, polymers with M_n s ranging from 11,500 to 31,100 g/mol (eqPS), M_w s ranging from 18,400 to 126,000 g/mol (eqPS), and dispersities ranging from 1.03 to 4.05 were obtained. They exhibited T_g s between -38 and 64 °C and initial decomposition temperatures ranging from 260 to 276 °C. Using the same procedure, Deng *et al.*³⁸ prepared crystallizable aliphatic thermoplastic NIPUs by reacting di(hydroxyethyl)hexane dicarbamate with triethylene glycol and tetraethylene glycol. The obtained polymers exhibited M_n s between 32,000 and 60,000 g/mol (eqPS), M_w s between 54,000 and 76,000 g/mol (eqPS), T_g s ranging from 11 to 28 °C, T_m s from 104 to 151 °C, and $T_{5\%}$ s from 237 to 268 °C. In another study, Deng *et al.*³⁹ prepared aliphatic thermoplastic NIPUs by reacting di(hydroxyethyl)hexane dicarbamate with PEGs (400, 600, 1000, and 1500). The obtained polymers exhibited T_g s between 12.4 and -40.4 °C, T_m s up to 149.8 °C, and $T_{5\%}$ s over 239.4 °C.

In this study, we examined the transurethane polycondensation of renewable DCs with PEG1500 as a soft segment for the first time in the presence or absence of BD as a chain extender (reaction 2). The Acme–Hardesty Co. recently produced fully biobased PEGs made from bagasse, which is the fibrous waste that remains after sugarcane stalks are crushed to extract their juice. BD can be produced through the chemical modification of succinic acid.⁴⁶

The polycondensation was conducted at 140 °C under neat conditions for 16 h. Transurethane polycondensation with a polyol oligomer as the monomer has never been described at less than 150 °C as far as we know. A continuous nitrogen flow was

applied to remove MeOH. TBD, DBTL, and K_2CO_3 were each used as catalysts at 0.1 equiv with respect to PEG1500. As far as we know, this is the first time DBTL has been used for this kind of polymerization. DBTL is one of the most used and famous catalysts in the classical and industrial PU field. PEG1500 and dicarbamates were used at stoichiometric proportions to offer the highest polymer molecular weights. Indeed, the use of dicarbamate in excess or in default led, as expected, to molecular weight limitations (Supporting Information). This was another divergence with reaction 1, in which the excess of di(hydroxyethyl) dicarbamate led to an increase in the hard segment's molecular weight and, theoretically, did not influence the molecular weight of the final polymer. However, Li *et al.*³⁵ and Deng *et al.*³⁹ observed a decrease in the polymer's molecular weight with increasing excess of di(hydroxyethyl)isophorone biscarbamate; this was probably due to the increase in the viscosity; which led to a limitation of the conversion. In our study, the increase in the hard segment's molecular weight was performed through the addition of BD at 0.0, 0.5, 1.0 or 1.5 equiv with respect to PEG1500. The reaction temperature was also increased to 150 or 160 °C to assess its influence on the polymer properties. In parallel, standard PU was prepared through the reaction of PEG1500 with HDI at 80 °C in the presence of DBTL as catalyst. The reaction was completed in 2 h. The obtained polymers were soluble in classical organic solvents and in aqueous and alcoholic media. Thus, they were solubilized in dichloromethane and then precipitated in petroleum ether. All of the materials were hard, and they exhibited a white color, except for PU7 and PU8, which were both yellowish.

The FTIR spectra of the prepared materials displayed bands mainly around 1720 and 3330 cm^{-1} , which arose from the stretching vibrations of the C=O and N–H bonds of the urethane groups, respectively. The FTIR spectrum of PU (PEG–HDI) was very close to the spectrum of PU1 and showed the total disappearance of the isocyanate band at 2270 cm^{-1} ; this demonstrated the end of the reaction.

The polymer molecular weights were assessed by SEC in dichloromethane with PMMA as a standard. The main results are depicted in Table I. Typical examples of the chromatograms are given in Figure 1. We observed that the M_w values were higher than 11,000 g/mol for materials prepared with TBD (PU1) or DBTL (PU6) as a catalyst. DBTL seemed to be as efficient as TBD in the catalysis of the transurethane reaction. However, with K_2CO_3 , the M_w value was around 7500 g/mol (PU5); the suggested that this catalyst was less efficient than TBD and DBTL at 140 °C. This was probably due to its low solubility in the medium. This result was consistent with our previous observations and indicated a good solubility and catalytic effect of K_2CO_3 at 200 °C, a temperature at which TBD could

Table I. Molecular Weights Determined by SEC for the Prepared NIPUs (PMMA Standard)

PU	DC	Temperature (°C)	Catalyst	PEG/BD/DC	M_w (g/mol)	Dispersity	Appearance ^a
PU1	C6	140	TBD	1:0:1	11,800	1.7	H, W
PU2	C6	140	TBD	1:0.5:1.5	14,800	1.9	H, W
PU3	C6	140	TBD	1:1:2	14,800	1.8	H, W
PU4	C6	140	TBD	1:1.5:2.5	11,600	1.9	H, W
PU5	C6	140	K ₂ CO ₃	1:0:1	7,500	1.6	H, W
PU6	C6	140	DBTL	1:0:1	11,300	1.7	H, W
PU7	C10	140	TBD	1:0:1	14,500	1.6	H, Y
PU8	Priamine 1074	140	TBD	1:0:1	14,300	1.6	H, Y
PU9	C6	150	TBD	1:0:1	17,200	1.8	H, W
PU10	C6	160	TBD	1:0:1	16,000	1.8	H, W
PEG1500	—	—	—	—	1,850	1.3	P, W
PU (PEG-HDI)	—	80	DBTL	1:0:1 ^b	12,600	1.2	H, W

^aH, hard material; P, powder; Y, yellowish; W, white.

^bHDI instead of DC.

not be used because of degradation.³¹ The increase in the temperature, from 140 °C (PU1) to 150 °C (PU9) and 160 °C (PU10), improved chain extension and lead to an increase in the M_w values from 11,800 to 17,200 and 16,000 g/mol, respectively. Furthermore, we observed an increase in M_w from 11,800 g/mol (PU1) to 14,800 g/mol (PU2 and PU3) when the BD content was increased from 0 to 0.5 and 1 equiv, respectively. However, the M_w value fell to 11,600 g/mol when BD was added at 1.5 equiv (PU4); this was probably due to the increase in the viscosity with the hard-segment content. This limited the conversion. This result was in agreement with those of Li *et al.*³⁵ and Deng *et al.*³⁹ PU7 based on dimethyl 1,10-decylenedicarbamate and PU8 based on DC of Priamine 1074 exhibited higher M_w values (14,500 and 14,300 g/mol, respectively) than their analog based on HDC (PU1). The standard polymer PU (PEG1500-HDI) exhibited and M_w value of 12,800 g/mol; this was close enough to the M_w value of PU1 to make a physical properties comparison possible.

The prepared polymers were then analyzed by ¹H-NMR in CDCl₃. The ¹H-NMR spectra of PU1 and its monomers are given in Figure 2 as typical examples. We observed the disappearance of the signal at 3.72 ppm, which corresponded to methylene groups in the α position to the terminal hydroxyl groups of PEG1500. We also observed the proton signals of the methylene group in the α position to the oxygen of the urethane links at 4.20 ppm when these protons belonged to the reacted PEG chain and at 4.06 ppm when they belonged to the reacted BD chain. The signals of methylene groups in the α position to the nitrogen of the urethane links were observed at 3.14. This signal also corresponded to analog protons in the methyl carbamate end groups. The methyl's signal of these end groups arose at 3.65 ppm and overlapped with the main signal of the PEG chain. Therefore, the integration of the peak at 3.14 ppm was always higher than the integration of the peak at 4.20 ppm (and 4.06 ppm). In addition, the chain-end contribution decreased with the polymer molecular weight (e.g., PU1, PU9, and PU10 in the Supporting Information). The peak of the proton linked to the nitrogen atoms of the urethane

function were observed around 4.90 ppm. PU8 based on Priamine 1074 exhibited a supplementary peak around 0.85 ppm; this arose from the protons of the methyl groups of the alkyl side chains. However, because the end-group signals were partially to totally overlapped with other ones, we could not accurately perform any molecular weight calculations. On the other hand, the absence of peaks around 3.25 ppm (CH₂ in the α position to the urea group) and in the region of 5.5–7.0 ppm (NH of urea) suggested that under our conditions, the back-biting side reaction that led to urea formation did not occur.

The thermal properties of the prepared polymers were assessed by DSC and are depicted in Table II. Typical examples of DSC thermograms are given in Figures 3 and 4. The starting PEG1500 was semicrystalline, and the T_g of its amorphous domains was not observed. The crystalline domain exhibited a T_m and a crystallization temperature (T_c) of 49 and 14 °C with enthalpies of 160 and 155 J/g, respectively. In general, after polymerization with dicarbamates, the enthalpy values fell; this suggested a decrease in the crystalline percentage of the PEG segments. The T_m values also

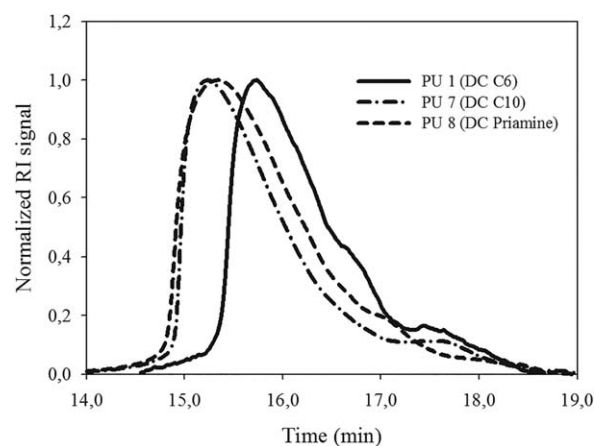


Figure 1. SEC chromatograms of PU1, PU7, and PU8. RI: refractive index.

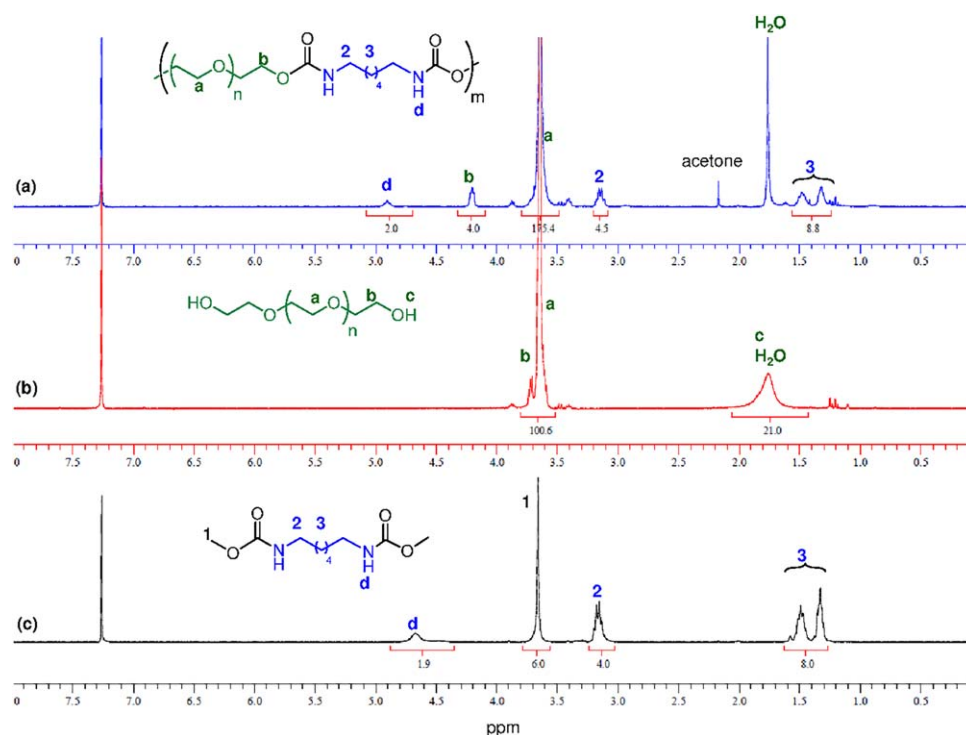


Figure 2. ^1H NMR spectrum in CDCl_3 of: (a) PU 1; (b) PEG1500; (c) Dimethyl 1,6-hexylenedicarbamate. [Color figure can be viewed at wileyonlinelibrary.com]

fell and ranged from 38 to 48 °C, whereas the T_c values were disparate and ranged from 11 to 35 °C. This tendency in the enthalpy and T_m values was also observed by Doseva *et al.*,¹⁰ who reacted PEG400, PEG600, and PEG1000 with isophorone diisocyanate and tolylene-2,4-diisocyanate. This result suggested a change in the allotropic system of the crystalline domain of PEG after polymerization. The T_g of the PEG soft segments within the prepared NIPUs materials was detectable by DSC only in some cases. Negative T_g s, ranging from −49 to −1 °C, were observed; this showed demonstrated elastomeric properties. For instance, PU2 and PU3 made with 0.5 and 1 equiv, respectively, of BD

exhibited T_g values of −48 and −49 °C, respectively. PU9 and PU10 prepared at 150 and 160 °C, respectively, displayed higher T_g values, that is, −1 and −2 °C, respectively. This result could be explained by their higher molecular weight (ca. 17,000 g/mol). PU8 prepared with dicarbamate of Priamine 1074 exhibited a medium T_g value of −30 °C. The ΔC_p (heat capacity at constant pressure) values ranged from 0.38 to 0.60 $\text{J g}^{-1} \text{ °C}^{-1}$ and were characteristic of aliphatic chains.

The crystalline domain of the hard segments was observed only when BD was used at 1.5 equiv toward PEG. It displayed a T_m and T_c of 133 and 85 °C, respectively, with weak enthalpies of

Table II. Thermal Properties of the Prepared NIPUs from the Second Cycle of the DSC Analysis

PU	T_m (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)	T_g (°C)	ΔC_p (J/g °C)	$T_{5\%}$ (°C)
PU1	46	30	126	122	—	—	325
PU2	38	11	92	87	−48	0.38	309
PU3	38	11	94	87	−49	0.43	302
PU4	45; 133	12; 85	60; 19	59; 14	—	—	237
PU5	46	28	134	133	—	—	287
PU6	46	30	118	111	—	—	310
PU7	48	35	129	121	—	—	309
PU8	46	3	109	97	−30	0.60	350
PU9	46	28	121	121	−1	0.54	311
PU10	45	22	118	111	−2	0.39	305
PEG1500	49	14	160	155	—	—	343
PU (PEG-HDI)	43	24	78	77	−9	0.42	285

ΔH_c , crystallization enthalpy.

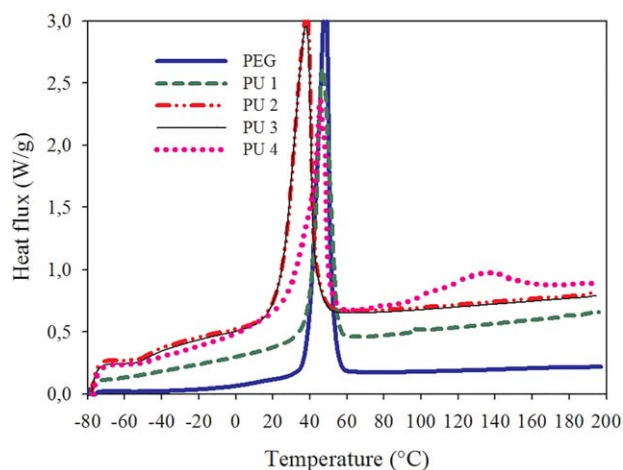


Figure 3. DSC thermograms of PEG1500 and PU1–PU4 (second heating). [Color figure can be viewed at wileyonlinelibrary.com]

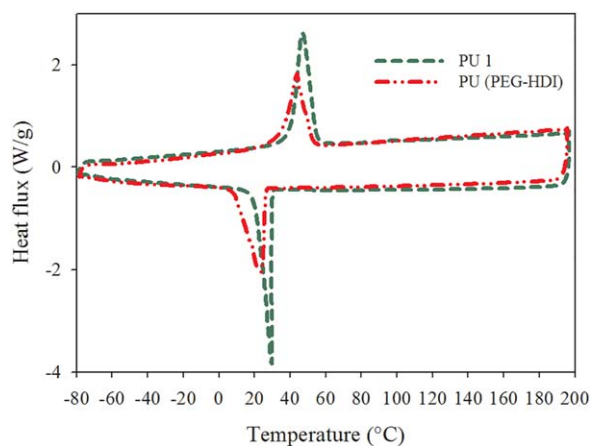


Figure 4. DSC thermograms (second cycle) of PU1 and PU (PEG–HDI). [Color figure can be viewed at wileyonlinelibrary.com]

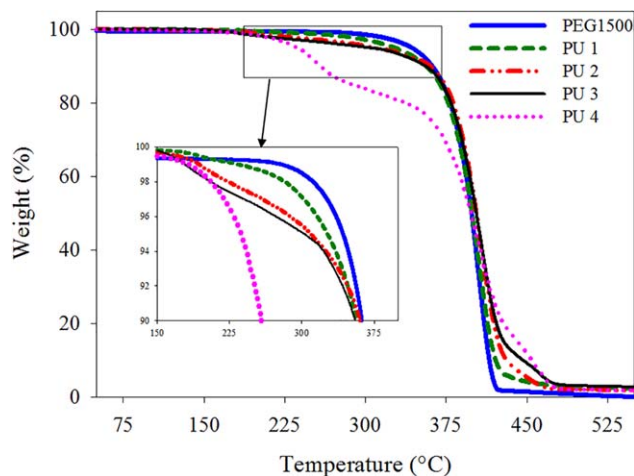


Figure 5. TGA thermograms of PEG1500 and PU1–PU4. [Color figure can be viewed at wileyonlinelibrary.com]

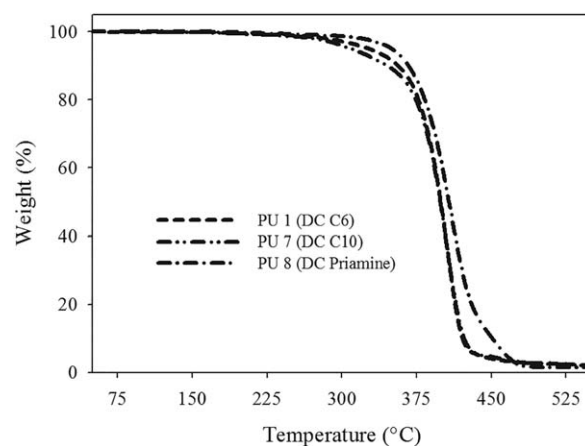


Figure 6. TGA thermograms of PU1, PU7, and PU8

19 and 14 J/g, respectively. However, the T_g values of these segments were not observed. These values were close to those of PU6-6 prepared elsewhere from HDC and 1,6-hexanediol ($T_m = 130^\circ\text{C}$, $T_c = 96^\circ\text{C}$).³¹

PU (PEG–HDI) prepared through the isocyanate approach displayed thermal properties that were close to those of its NIPU analogs (PU1, PU9, and PU10), which theoretically had the same chemical structures. Nevertheless, it exhibited lower enthalpies; the syndicated a lower crystalline percentage of the PEG segments. This result suggests that the PU chains were less regular than the NIPU chains. Indeed, during PU synthesis, isocyanate groups could react with urethane groups to afford allophanate groups; this led to side-chain formation and/or crosslinking. For the NIPUs, this side reaction could not occur under the operating conditions.

The thermal stability of the prepared polymers was assessed by TGA under a nitrogen atmosphere. The $T_{5\%}$ values are given in Table II. Typical TGA thermograms are given in Figures 5–7. These polymers displayed good thermal stability up to 200°C , with $T_{5\%}$ ranging from 237 to 350°C . We observed a decrease in the thermal stability with the initial amount of BD within the monomer mixture, that is, with the urethane linkage content

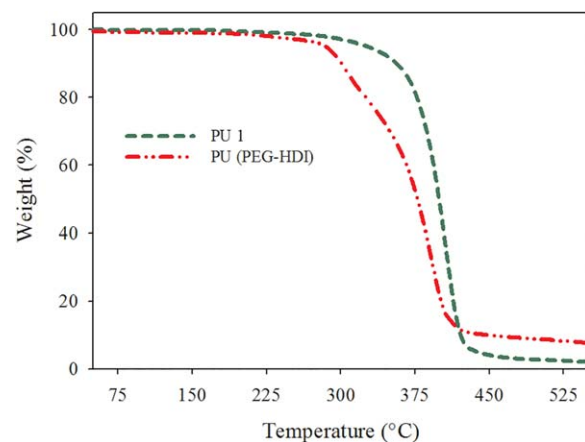


Figure 7. TGA thermograms of PU1 and PU (PEG–HDI). [Color figure can be viewed at wileyonlinelibrary.com]

within the final material (PU1–PU4). Therefore, PU4 exhibited a thermal stability similar to those of the NIPUs analogs made from reaction 1.^{36–39} Indeed, the degradation of urethane linkages occurred before the degradation of the hydrocarbon chains; this led to the release of small molecular fragments.⁴⁹ The PU thermal stability also increased with the repeating unit's molecular weight, that is, the molecular weight between urethane linkages. Thus, PU7 (based on DC C10) and PU1 (based on DC C6) exhibited quite similar thermal stabilities, whereas PU8 (based on DC of Priamine 1074) was the most thermally stable. Finally, PU (PEG–HDI) was less thermally stable than its PU1 analog. This result could be explained by the presence of allophanate links in the PU (PEG–HDI), for which degradation occurred before the degradation of urethane groups.

CONCLUSIONS

In this article, we have reported the synthesis with the transurethanization approach of new thermoplastic NIPU elastomers based on PEG. DCs were produced by reaction of renewable diamines with an excess of DMC. Then, bulk polycondensation was performed with PEG and BD in several proportions at temperatures ranging from 140 to 160 °C. Under these conditions, TBD and DBTL exhibited more catalytic efficiency than K₂CO₃. Overall, the prepared polymers exhibited molecular weights of up to 10,000 g/mol and displayed good thermal stabilities (>200 °C). The obtained NIPUs were semicrystalline. The T_g and T_m values of the soft segments (PEG) ranged from –49 to –1 °C and from 38 to 49 °C, respectively. The T_g and T_m values of the hard segment were not observed, except for PU4 (T_m = 133 °C), which contained the highest amount of BD. In a comparison to PU's analogs, the prepared NTPUs were more crystalline and more thermally stable. This was due to absence of the allophanate side reaction, which generates chain irregularity and side-chain formation. In terms of applications, through the reaction with crosslinking agents (trimethyl carbamates) or the physical or chemical addition of crosslinkable end groups, the prepared green and potentially fully biosourced polymers could be considered precursors of PU hydrogels, which are thoroughly used as biomaterials.^{1–7} In the current form, they can be used as water-soluble surfactants⁵⁰ and additives for waterborne coatings.⁵¹

ACKNOWLEDGMENTS

The authors thank European Union, the Centre de Recherche Universitaire Normand de Chimie, and the Haute Normandie region for their financial support.

REFERENCES

1. Divakaran, A. V.; Torris, A.; Lele, A. K.; Badiger, M. V. *Polym. Int.* **2015**, *64*, 397.
2. Cipolatti, E. P.; Moreno-Pérez, S.; de Andrade Souza, L. T.; Valério, A.; Guisán, J. M.; de Araújo, P. H. H.; Sayer, C.; Ninow, J. L.; de Oliveira, D.; Costa Pessela, B. J. *Mol. Catal. B* **2015**, *122*, 163.
3. Park, D.; Wu, W.; Wang, Y. *Biomaterials* **2011**, *32*, 777.
4. Mo, F.; Zhou, F.; Chen, S.; Yang, H.; Ge, Z.; Chen, S. *Polym. Int.* **2015**, *64*, 477.
5. Ikeda, Y.; Kohjiya, S.; Takesako, S.; Yamashita, S. *Biomaterials* **1990**, *11*, 553.
6. Bonfil, M.; Sirkecioglu, A.; Bingol-Ozakpinar, O.; Uras, F.; Güner, F. S. *J. Appl. Polym. Sci.* **2014**, *131*, DOI: 10.1002/app.40590.
7. Ren, Z.; Chen, G.; Wei, Z.; Sang, L.; Qi, M. *J. Appl. Polym. Sci.* **2013**, *127*, 308.
8. Xie, Z.; Lu, C.; Chen, X.; Chen, L.; Hu, X.; Shi, Q.; Jing, X. *Eur. Polym. J.* **2007**, *43*, 2080.
9. Yen, M.-S.; Tsai, P.-Y.; Hong, P.-D. *J. Appl. Polym. Sci.* **2007**, *105*, 1391.
10. Doseva, V.; Shenkov, S.; Vasilev, S.; Baranovsky, V. Y. *J. Appl. Polym. Sci.* **2004**, *91*, 3651.
11. Fonseca, L. P.; Trinca, R. B.; Felisberti, M. I. *J. Appl. Polym. Sci.* **2016**, *133*, DOI: 10.1002/app.43573.
12. Cao, Q.; Liao, L.; Xu, H. *J. Appl. Polym. Sci.* **2010**, *115*, 2228.
13. Askinadze, N.; Gluz, E.; Ziv, O.; Mizrahi, D. M.; Margel, S. *Polymer (Guildf)* **2013**, *54*, 2926.
14. Kébir, N.; Campistron, I.; Laguerre, A.; Pilard, J. F.; Bunal, C. *J. Appl. Polym. Sci.* **2011**, *122*, 1677.
15. Maisonneuve, L.; Lamarzelle, O.; Rix, E.; Grau, E.; Cramail, H. *Chem. Rev.* **2015**, *115*, 12407.
16. Panwiriyarat, W.; Tanrattanakul, V.; Pilard, J.-F.; Burel, F.; Kébir, N. *J. Appl. Polym. Sci.* **2016**, *133*, DOI: 10.1002/app.42943.
17. Kreye, O.; Mutlu, H.; Meier, M. A. R. *Green Chem.* **2013**, *15*, 1431.
18. Nohra, B.; Candy, L.; Blanco, J.-F.; Guerin, C.; Raoul, Y.; Mouloungui, Z. *Macromolecules* **2013**, *46*, 3771.
19. Duval, C.; Kébir, N.; Jauseau, R.; Burel, F. *J. Polym. Sci. Part A: Polym. Chem.* **2016**, *54*, 758.
20. Kathalewar, M. S.; Joshi, P. B.; Sabnis, A. S.; Malshe, V. C. *RSC Adv.* **2013**, *3*, 4110.
21. Camara, F.; Benyahya, S.; Besse, V.; Boutevin, G.; Auvergne, R.; Boutevin, B.; Caillol, S. *Eur. Polym. J.* **2014**, *55*, 17.
22. Fleischer, M.; Blattmann, H.; Mülhaupt, R. *Green Chem.* **2013**, *15*, 934.
23. Kathalewar, M.; Sabnis, A.; D'Mello, D. *Eur. Polym. J.* **2014**, *57*, 99.
24. Cornille, A.; Dworakowska, S.; Bogdal, D.; Boutevin, B.; Caillol, S. *Eur. Polym. J.* **2015**, *66*, 129.
25. Van Velthoven, J. L. J.; Gootjes, L.; Van Es, D. S.; Noordover, B. A. J.; Meuldijk, J. *Eur. Polym. J.* **2015**, *70*, 125.
26. Bigot, S.; Daghrir, M.; Mhanna, A.; Boni, G.; Pourchet, S.; Lecamp, L.; Plasseraud, L. *Eur. Polym. J.* **2016**, *74*, 26.
27. Cornille, A.; Serres, J.; Michaud, G.; Simon, F.; Fouquay, S.; Boutevin, B.; Caillol, S. *Eur. Polym. J.* **2016**, *75*, 175.
28. More, A. S.; Gadenne, B.; Alfes, C.; Cramail, H. *Polym. Chem.* **2012**, *3*, 1594.

29. More, A. S.; Maisonneuve, L.; Lebarbé, T.; Gadenne, B.; Alfos, C.; Cramail, H. *Eur. J. Lipid Sci. Technol.* **2013**, 115, 61.
30. More, A. S.; Lebarbé, T.; Maisonneuve, L.; Gadenne, B.; Alfos, C.; Cramail, H. *Eur. Polym. J.* **2013**, 49, 823.
31. Duval, C.; Kébir, N.; Charvet, A.; Martin, A.; Burel, F. *J. Polym. Sci. Part A: Polym. Chem.* **2015**, 53, 1351.
32. Unverferth, M.; Kreye, O.; Prohammer, A.; Meier, M. A. R. *Macromol. Rapid Comm.* **2013**, 34, 1569.
33. Martin, A.; Lecamp, L.; Labib, H.; Aloui, F.; Kébir, N.; Burel, F. *Eur. Polym. J.* **2016**, 84, 828.
34. Rokicki, G.; Piotrowska, A. *Polymer* **2002**, 43, 2927.
35. Li, S.; Zhao, J.; Zhang, Z.; Zhang, J.; Yang, W. *Polymer* **2015**, 57, 164.
36. Li, S.; Sang, Z.; Zhao, J.; Zhang, Z.; Cheng, J.; Zhang, J. *Eur. Polym. J.* **2016**, 84, 784.
37. Li, S. Q.; Zhao, J. B.; Zhang, Z. Y.; Zhang, J. Y.; Yang, W. T. *RSC Adv.* **2014**, 4, 23720.
38. Deng, Y.; Li, S. Q.; Zhao, J. B.; Zhang, Z. Y.; Zhang, J. Y.; Yang, W. T. *RSC Adv.* **2014**, 4, 43406.
39. Deng, Y.; Li, S. Q.; Zhao, J. B.; Zhang, Z. Y.; Zhang, J. Y.; Yang, W. T. *Chin. J. Polym. Sci.* **2015**, 33, 880.
40. Deepa, P.; Jayakannan, M. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, 45, 2351.
41. Deepa, P.; Jayakannan, M. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, 46, 2445.
42. Dongdong, P.; Hengshui, T. *J. Appl. Polym. Sci.* **2015**, 132, DOI: 10.1002/app.41377
43. Liu, B.; Tian, H.; Zhu, L. *J. Appl. Polym. Sci.* **2015**, 132, DOI: 10.1002/app.42804.
44. Choi, J. C.; He, L. N.; Yasuda, H.; Sakakuda, T. *Green Chem.* **2002**, 4, 230.
45. Ballini, R.; Fiorini, D.; Maggi, R.; Righ, P.; Sartori, G.; Sartori, R. *Green Chem.* **2003**, 5, 396.
46. Harmsen, P. F. H.; Hackmann, M. M.; Bos, H. L. *Biofuels Bioprod. Bioref.* **2014**, 8, 306.
47. Archer, R.; Diamond, G. M.; Dias, E. L.; Murphy, V. J.; Petro, M.; Super, J. D. W. O. Pat. 2013090031 A2 20130620 (**2013**).
48. Wu, S.; Li, X.; Ye, X.; Li, J.; Wang, N.; Lu, Q.; Zhu, R.; Yan, S.; Wang, J. C. N. Pat. 101628875 A 20100120 (**2010**).
49. Kébir, N.; Campistron, I.; Laguerre, A.; Pilard, J.-F.; Bunel, C.; Couvercelle, J.-P. *e-Polymers* **2006**, 048, 1.
50. Ismail, E. A. *J. Appl. Polym. Sci.* **1998**, 68, 1531.
51. Kalele, M. H.; Zhu, Y.; Mulenga, M. C. *Int. J. Chem.* **2011**, 3, 88.