Preparation of Dicarbamate Monomers

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Abstract

Surface anomalies on aircraft wings can cause increased drag resulting in a series of problems ranging from loss of fuel efficiency to unsafe flying conditions. This study focused on synthesizing a non-toxic dicarbamate monomer that can be used to prepare polymer coatings to prevent material accretion. The dicarbamate monomer was prepared following a literature procedure and its structure and purity determined by spectral methods. Polyurethanes synthesized from the dicarbamate monomer and diols were obtained in low yield and determined to be low molecular weight by inherent viscosity, The reaction of the dicarbamate monomer with a diamine afforded a polyurea in high yield. The high level of interchain hydrogen bonding present in the polyurea prevented dissolution in solvent to determine inherent viscosity.

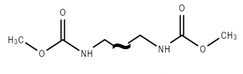
Background

Polyurethanes

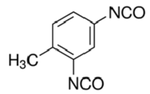
- Alternating copolymer structure
  - Hard-block component
  - Soft- block component
  - Combined they provide rigidity and flexibility
- Typically made using isocyanates, which are toxic
- To reduce toxicity, a dicarbamate was substituted for the diisocyanate

Hard-block component provides rigidity

Soft-block component provides flexibility

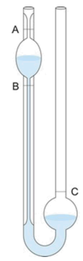


dicarbamate



diisocyanate group - 2 NCO groups on a toluene molecule.

- **Polymer synthesis**
  - React the dicarbamate monomer with diols in an appropriate solvent
  - Indirectly assess molecular weight using inherent viscosity, dL/g
  - A high inherent viscosity implies high molecular weight
  - Make coatings with polymer and test physical properties



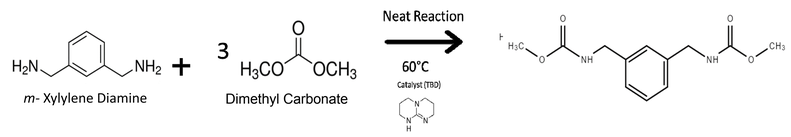
Ostwald viscometer

$$\eta_{inherent} = \frac{\ln(\frac{t}{t_0})}{c}$$

where
t = time, in seconds, for solution to flow through the viscometer
t_0 = time, in seconds, for solvent to flow through the viscometer
c = concentration, g/dL, of polymer in solvent

Materials and Methods

Hard-block Synthesis



m- Xylylene Diamine + 3 Dimethyl Carbonate

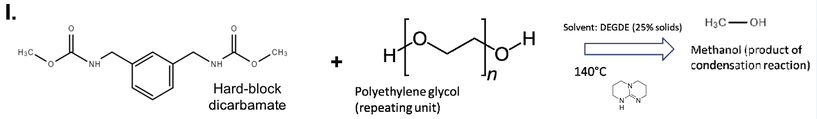
Purification

- Determined the best solvent for recrystallization
- The monomer was then characterized by AFTIR and FT-NMR to verify the structure and assess purity

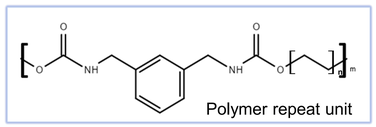
Solvent	Soluble at RT	Soluble with heat	Re-crystalize out
Ethyl Acetate	No	Yes	No - oils
Cyclohexanone	No	Yes	No
Cyclohexane	No	Yes	Yes – low solubility
Hexanes	No	No	Didn't dissolve
Methanol	No	Yes	No
Toluene	No	Yes	Yes – Best one

Polyurethane Synthesis

I.

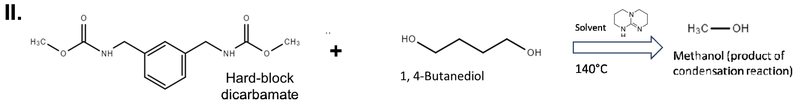


Hard-block dicarbamate + Polyethylene glycol (repeating unit)

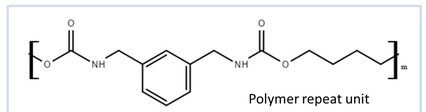


- Remained soluble in water rather than precipitating
- The diol was a PEG oligomer with an average number average molecular weight of 400 g/mol
- May have led to a stoichiometric imbalance

II.

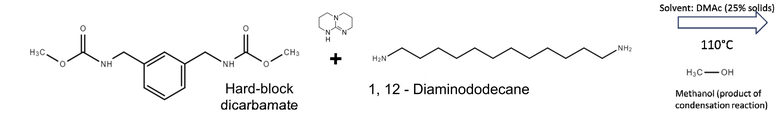


Hard-block dicarbamate + 1, 4-Butanediol

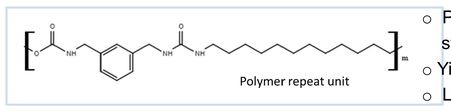


- Reaction performed in two solvents - diethylene glycol diethyl ether and N,N- dimethylacetamide
- Inherent viscosity measurements implied low molecular weight
- Polymer made in N,N- dimethylacetamide (0.09 dL/g) was lower than the one in diethylene glycol diethyl ether (0.14 dL/g)

Polyurea Synthesis



Hard-block dicarbamate + 1, 12 - Diaminododecane

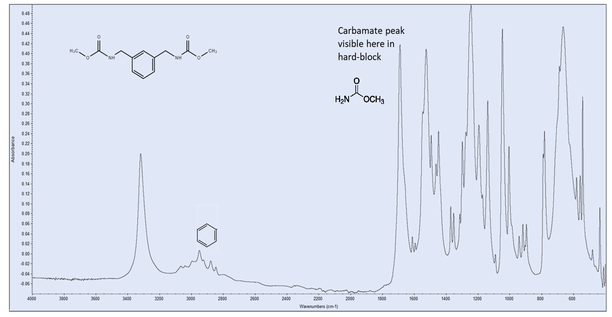


- Precipitated polymer by addition to stirred water
- Yield was 93% after drying in air
- Low solubiltiy in solvents prevented inherent viscosity measurements

Results and Conclusions

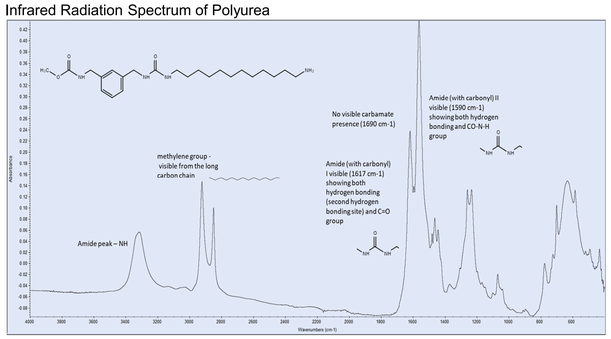
FTIR spectroscopy

FTIR Spectrum of Dicarbamate Hard-block



- Carbonyl peak at ~1690 cm^{-1} associated with carbamate
- Absence of carbonyl peak at ~1760 cm^{-1} associated with DMC
- Suggests reaction had gone to completion

Infrared Radiation Spectrum of Polyurea



- Carbamate peak at ~ ~1690 cm^{-1} no longer present
- Replaced by new peaks (Amide I and II) associated with amide carbonyl of the urea group

Accomplishments

- Synthesis and purification of hard-block dicarbamate
- Confirmed structure by FT-NMR and FTIR
- Polymers were prepared and characterized by inherent viscosity

Future Direction

- Prepare polyurea from other diamines
- Molecular weight control using the Carothers's equation
- Characterize polymers spectrally and by other techniques (e.g., contact angle goniometry)
- Fabricate coatings on aluminum substrates
- Characterize impact properties of coatings
- Characterize material accretion properties

Acknowledgments

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