

Kinetic and thermodynamic studies of the formation of a polyurethane based on 1,6-hexamethylene diisocyanate and poly(carbonate-*co*-ester)diol

B. Fernandez d'Arlas^a, L. Rueda^a, P.M. Stefani^b,
K. de la Caba^a, I. Mondragon^a, A. Eceiza^{a,*}

^a "Materials+Technologies" Group, Department of Chemical and Environmental Engineering, Eskola Politeknikoa/Escuela Politécnica, Euskal Herriko Unibertsitatea, Pza. Europa 1, 20018 Donostia-San Sebastián, Spain

^b Research Institute of Material Science and Technology (INTEMA), Engineering Faculty, Mar del Plata University, Juan B. Justo 4302, 7600 Mar del Plata, Argentina

Received 6 February 2007; received in revised form 26 March 2007; accepted 31 March 2007

Available online 5 April 2007

Abstract

This paper presents the kinetic and thermodynamic characterization of a non-catalyzed reaction between poly(hexamethylene carbonate-*co*-caprolactone)diol (PHMC-*co*-PCL) and aliphatic hexamethylene diisocyanate (HDI) with a stoichiometric functional concentration, using both isothermal and dynamic differential scanning calorimetry, DSC, as well as Fourier transform infrared spectroscopy, FT-IR. DSC data were fitted using a Kamal autocatalytic equation. Model-free-isoconversional methods were also applied to analyse the conversion dependence of the global activation energy. This relation was used to predict the reaction conversion versus time pattern at different temperatures and to compare it with that of the model approach. Kinetic modelling and model-free analysis successfully described the conversion versus time curves. The reaction can be divided in two different paths: the forward path and the autocatalyzed one. Results corroborated that autocatalysis is promoted by the urethane group. Activation energies for both reaction paths have been found to be higher than those presented in the literature for aromatic diisocyanate systems, which explains the lower reaction rate of the presented system.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Aliphatic polyurethane; Kinetics; Autocatalysis; Kamal; Model-free-isoconversional

1. Introduction

Polyurethanes are very versatile polymers which allow creating new promising materials. This is mainly due to the way they are synthesized and the wide range of different components that can be used to form diverse polyurethanes. Segmented thermoplastic polyurethane elastomers (STPUEs) based on poly(ester)urethanes and poly(carbonate)urethanes have been claimed to be promising biodegradable materials with potential utilities in biomedical sciences applications, as long term medical implants, mainly in blood contact devices [1–6]. These polyurethanes have received great attention as they possess a

broad range of chemical and physical properties, good biocompatibility and can be designed to degrade in biological environments due to the possibility of easily varying their chemical composition. In previous work, commercially synthesized polyurethanes were prepared with no completely biocompatible precursors [1,5,6]. In this work, hexamethylene diisocyanate, which is claimed as not toxic amine producer during degradation of the corresponding polyurethanes [1,6], has been used. No catalyst was employed for avoiding biocompatibility problems of the material.

Knowledge of kinetic parameters of a reactive resin is essential on the design and processing of polymer and composite technologies. Kinetic prediction of the cure pattern over a wide temperature range is also of interest. The present polyurethane addition reaction was followed by Fourier transform infrared spectroscopy (FT-IR) and by differential scanning calorimetry

* Corresponding author.

E-mail address: arantxa.eceiza@ehu.es (A. Eceiza).