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Calorimetric investigation of the reactivities of polyether macrodiols and glycerol with 4,4′-diphenylmethane diisocyanate (MDI)[1]

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Abstract

The rates of reaction of glycerol and two polyether macrodiols, differing in molecular weight by a factor of 6, with a commercial grade of liquid polymeric 4,4′-diphenylmethane diisocyanate (MDI) were determined using data from reaction calorimetric studies. Rate constants were determined for the reactions of each of the macrodiols and glycerol with the isocyanate. The reactivities of the primary hydroxyl groups in glycerol were similar to those of the macrodiols. The more sterically hindered secondary hydroxyl group in glycerol was found to have a reactivity one third that of the primary hydroxyl groups.

Keywords: 4,4′-Diphenylmethane diisocyanate; Glycerol; Polyether macrodiol; Rate constant; Reaction calorimetry

1. Introduction

The physical properties of polyurethanes depend both upon the structural units used for their construction, namely the diols, triols and isocyanates used for their preparation, and also upon the way in which these structural units are combined together during synthesis [1]. The synthetic procedure used can determine crucial aspects of the polymer structure, such as size and sequencing of hard and soft blocks. During the scale-up and optimisation of polymerisation processes for commercial manufacture, one of the key objectives should be to understand how the operating variables, such as

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temperature, addition rates, catalyst concentration, agitation, pressure, etc., influence the final product properties [2]. The preparation of polyurethanes is an exothermic process having reaction enthalpies typically in the range -80 to $-90\,\mathrm{kJ\,mol^{-1}}$ [3,4]. The advent of commercial reaction calorimeters has made this experimental method very attractive for scale-up investigations involving this type of chemistry.

In this paper we describe the use of reaction calorimetry to provide thermodynamic and kinetic data for the scale-up and optimisation of a polyurethane synthesis, involving the uncatalysed reaction product of a commercial grade of liquid polymeric 4,4′-diphenylmethane diisocyanate (MDI) with two polyether macrodiols and glyce- rol.

2. Materials

The polymeric 4,4′-diphenylmethane diisocyanate (a commercial MDI mainly consisting of the 4,4′-diisocyanate, but also containing some 2,4′-diisocyanate, some triisocyanate and some polyisocyanate) and both polyether macrodiols were obtained from commercial suppliers. The polymeric MDI was used as received. The polyether macrodiols were dried to water contents of less than 0.2% w/w by heating to approximately 80°C under reduced pressure. Glycerol was obtained from Aldrich Chemical Co.

The two polyether macrodiols were both poly(oxyethylene) chain capped and differed from each other only in their molecular weight, the higher molecular weight polyol being approximately 6 times that of the other.

3. Experimental

The polyurethane synthesis was studied using a Mettler RC1 reaction calorimeter fitted with the AP01 2-litre reaction vessel, glass anchor stirrer and glass temperature and calibration probes. Automatic liquid dosing was controlled by a Mettler RD10 dosing controller linked to a Prominent B 06.012 diaphragm pump and a Mettler PM4600 balance. The temperature of dosed material was sensed by a platinum resistance thermometer in the dosing head. This thermometer was interfaced to the RD10 and its measurements used to calculate the heat required to bring material being dosed to the temperature of the calorimeter contents.

The polymer synthesis was conducted by charging the polymeric MDI to the reaction vessel at 40°C and dosing a mixture of the polyols and glycerol to the isocyanate evenly over a period of 15 min. The isocyanate was in an approximately 4-fold molar excess compared to the hydroxyl-containing components. The calorimeter was operated in adiabatic mode, the heat of reaction being allowed to raise the temperature of the reaction mixture. In the commercial process, the synthesis as described above is the first stage of a multistage process.

Heat capacity data were determined by 5°C temperature ramps conducted at a rate of $0.25\,^{\circ}\mathrm{C\,min^{-1}}$. Heat transfer coefficients were determined by 20 minute calibrations with an approximately 20-W electrical heater.

The first calorimetric run was performed on the standard formulation in the same way as a normal polymer synthesis. The results of this first experiment led to separate studies of the reactivities of the individual hydroxyl-containing components with the polymeric MDI. These were conducted in experiments designed to model the reaction conditions in the later stages of the process. The experiments consisted of firstly charging the reaction vessel with the usual amount of polymeric MDI, then dosing 70% of the standard polyol and glycerol mixture required by the formulation, and allowing this to react under isothermal control (60°C) to completion. Finally a quantity of the individual polyol or glycerol (whichever was the subject of the particular experiment), equivalent in molar terms to the 30% of polyol/glycerol mixture not added in the first addition, was then introduced to the calorimeter and allowed to react under adiabatic conditions from a starting temperature 60°C.

4. Results and discussion

The results of specific heat capacity and heat transfer coefficient determinations over the temperature range studied are shown graphically in Fig. 1.

Evaluations of the heat flow data from the polymer synthesis were made using the calorimeter evaluation software version 3.2. The heat flow equation was set to

$$Q_r = Q_{flow} + Q_{accu} + Q_{dos} + Q_{loss}$$

where Q_r is the rate of heat generation of the chemical reaction, Q_{flow} is the heat flow through the calorimeter vessel wall, Q_{acc} is the heat stored within the reaction mass due to increasing temperature, Q_{dos} is the heat input due to reagents being added, and Q_{loss} is the heat loss to the surroundings. The default value for Q_{loss} was used. Integral baselines were used throughout.

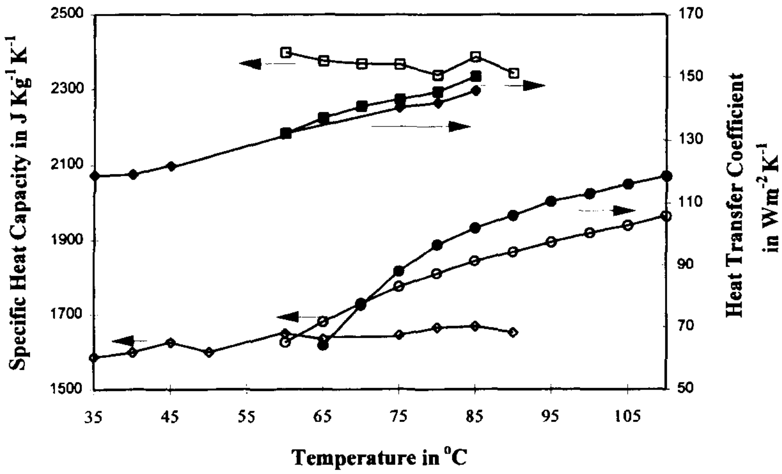

Fig. 1. Specific heat capacity and heat transfer coefficient determinations for MDI (◇,◆), polyol mixture (□,■), and reaction product (○,●).

The heats of reaction determined from evaluations of both the initial calorimetric run with mixed polyol/glycerol, and the subsequent runs with the individual hydroxyl-containing components, are given in Table 1. These values, normalised to the enthalpy change per mole of reaction, are within the expected range [3,4].

Evaluation of the initial calorimetric run examining the standard polymer synthesis gave the conversion profile for isocyanate shown in Fig. 2. The most notable feature of this conversion curve is the relatively slow approach to 100% conversion. This was of concern as it indicates the need for a long (and expensive) processing time and, in the case of a multicomponent system like this one, the presence of a component which is slow to react. Furthermore, the extent of reaction of this slowly reacting component could strongly influence the final product properties.

The conversion profile in Fig. 2 was obtained by equating the heat released by the reaction directly to the extent of reaction. With a multicomponent system, such as the one under investigation, this would be strictly true only if the heats of reaction for each of the hydroxyl-containing species were exactly the same. The results in Table 1 show that for the two polyether macrodiols and glycerol used in this work the heats of

Table 1
Heats of reaction determined from calorimetry experiments expressed relative to the amount of isocyanate functional groups consumed

Reactant	ΔH/kJ mol^{-1}
Mixed polyol	-80
Glycerol	-69
High molecular weight macrodiol	-82
low molecular weight macrodiol	-80

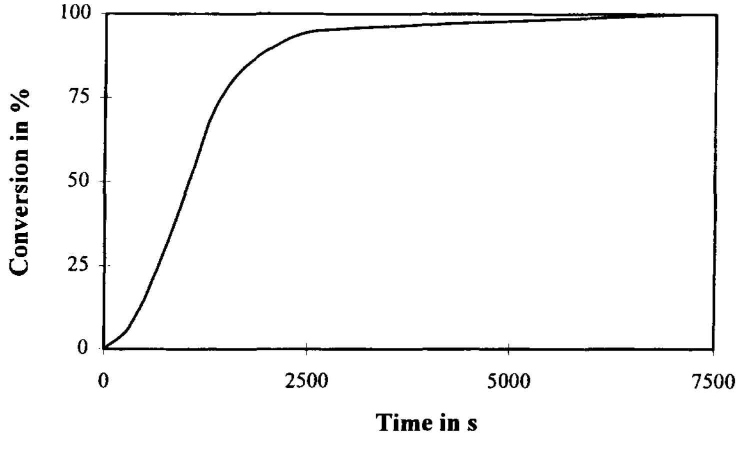

Fig. 2. Conversion profile for the reaction of the polymeric isocyanate (MDI) with the polyol mixture.

reaction differ by between 3 and 19%. These differences are not large enough to explain the slow approach to complete reaction indicated by the calorimetric data.

The observation of a long "tail" to the reaction (Fig. 2) led directly to the investigation of the reactivities of individual components, in the hope of identifying which component(s) was responsible for the slow reaction. To mimic the chemical environment of the later stages of the polymerisation, each hydroxyl-containing component was studied in reaction with an isocyanate-rich adduct of the polymeric MDI and the polyether/glycerol mixture. This isocyanate-rich adduct was made by reacting the normal amount of polymeric MDI with 70% of the polyol/glycerol mixture normally required by the formulation. The conversion profiles for these experiments are shown in Fig. 3. Both glycerol and the higher molecular weight polyether diol show slow conversions compared to the lower molecular weight polyether diol. However, it is not appropriate to compare directly the conversion profiles from these experiments to identify the slow reaction present in the commercial polymer synthesis. The nature of the 'individual component experiments' was to use the same molar quantity of each hydroxyl-containing component in each individual experiment. Because glycerol and the high molecular weight polyether macrodiol have very different molecular weights the only fair comparison of their reactivity can come from comparing reaction rate constants.

To obtain the individual rate constants for each of the reactions of interest, the conversion profiles obtained from the calorimetric experiments performed on the individual hydroxyl-containing components (Fig. 4) were curve fit against kinetic schemes using RATE software (BatchCAD Ltd., Newcastle). The reaction schemes used in the curve fitting consisted of the reaction of isocyanate with macrodiol hydroxyl units, with water, and with the hydroxyl units of glycerol. The best fit for glycerol was obtained when the primary and secondary hydroxyl groups in this molecule were allowed to have different reactivities. During the curve fitting procedure it became clear that the small temperature ranges covered in the experiments (between 10 and 17°C)

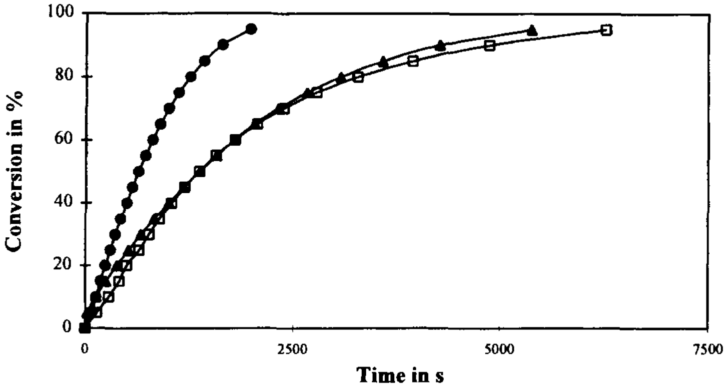

Fig. 3. Conversion profiles for low molecular weight macrodiol (●), high molecular weight macrodiol (▲), and glycerol (□), with the isocyanate-rich adduct.

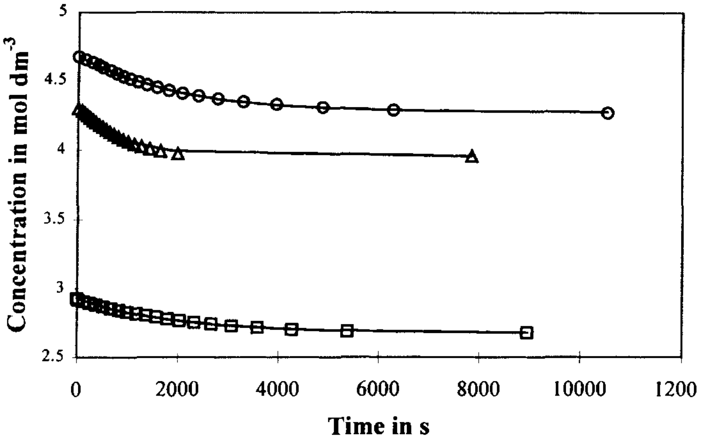

Fig. 4. Isocyanate concentration data (○, △, □) from calorimetric runs and best fit kinetic curves—for the glycerol (○), low molecular weight polyether macrodiol (△), and high molecular weight polyther macrodiol (□) reactions with the isocyanate-rich adduct.

were insufficient to enable activation energies to be determined reliably. The closeness of fit was almost independent of the activation energies chosen. Consequently an activation energy of 50 kJ mol^{-1}, taken from literature data[1, 5], was used in all cases.

Both the polyols and the glycerol used in the experimentation contained a small amount of water. In the curve fitting, the analytically determined water content was used to calculate the starting concentration of water in the reacting system. Water was a minor component in all cases and was not the reaction of interest. Nevertheless, its presence was recognised in the reaction scheme for completeness. The levels of water present were so small that the inclusion or exclusion of the water reaction in the curve fitting had little influence on the results.

Each of the 3 experiments (glycerol, and high and low molecular weight polyether macrodiol) was initially curve fit using a procedure which allowed all the pre-exponential factors in the rate constant expressions to vary, but which fixed the activation energies at a value of 50 kJ mol^{-1}. As each experiment involved a small amount of reaction of water and isocyanate, these 3 initial curve fittings gave 3 separate pre-exponential factors for the water : isocyanate reaction. For consistency, an average value for this pre-exponential factor was calculated and reintroduced into the curve fitting programme as a fixed value. The curve fitting procedure was then rerun for the 3 sets of experimental data to obtain the best fit curves shown in Fig. 4. The rate constants derived from these best fits are shown in Table 2. These compare favourably with values for similar reactions determined by other methods [1, 5, 6].

The rate constants obtained from curve fitting the calorimetric data show the secondary hydroxyl groups in glycerol to have considerably lower reactivity than any of the other hydroxyl groups present in the system. It is this component of the formulation which is responsible for the very slow approach to complete reaction in the polymer synthesis.

Table 2
Rate constants at 60°C for reactions with the isocyanate-rich prepolymer adduct determined by curve fitting calorimetric data

Reactant	$10^4 k/\mathrm{dm^3\,mol^{-1}\,s^{-1}}$
Glycerol: Primary hydroxyl	2.1
Secondary hydroxyl	0.72
High molecular weight macrodiol	1.8
low molecular weight macrodiol	2.7
Water	2.0

The low reactivity of the secondary hydroxyl group in glycerol has strong implications for a reproducible commercial process. The extent to which the secondary hydroxyl groups are incorporated into the isocyanate-terminated prepolymer will determine the functionality of the prepolymer and consequently, following further processing, the crosslink density and physical properties of the product. The better understanding of the kinetics of the process provided by the calorimetric study can be used to lead to a more robust approach to the synthesis. For example, it may be considered worthwhile investigating an alternative addition regime for the polymer synthesis, in which the glycerol is added earlier than the polyether macrodiols so that it may react under the most favourable reaction conditions of high isocyanate concentration. This could be investigated initially by reaction modelling using the kinetic data obtained in this investigation to quickly test the validity of the approach, and then confirmed by a calorimetric experiment. Alternatively, reformulation may be required in which glycerol is replaced by a triol which has hydroxyl groups of more similar reactivity.

The two polyether macrodiols were identical except in molecular weight, both being poly (oxyethylene) capped. The factor of 6 change in molecular weight has lead to a factor of 1.5 change in reactivity, which is most likely to arise from the difference in chain length and mobility of the chain in the reaction medium. The primary hydroxyl groups of glycerol have a reactivity intermediate between those of the two polyether macrodiols. Here a balance of steric and inductive effects must be at work, resulting in the relatively mobile glycerol molecule having a lower reactivity than the low molecular weight polyether macrodiol.

5. Conclusions

The reactivities of the primary and secondary hydroxyls in glycerol with a commercial MDI have been determined. The sterically hindered secondary hydroxyl groups in glycerol have a reactivity approximately one third of those of the primary hydroxyl groups in the same molecule. This has important processing implications for polyurethane preparations using this triol.

The influence of molecular weight on the reactivity of the macrodiols with the commercial polymeric MDI is a reduction in reactivity with increase in molecular weight. However, this is not as significant an effect as the difference in reactivity between primary and secondary hydroxyls in glycerol.

The component responsible for the long reaction tail in the polymer synthesis was identified as the secondary hydroxyl group in glycerol. This knowledge is vital to the successful development of such a polymer synthesis, as the extent to which the glycerol is fully incorporated into the polymer at the time the next stage of the process is commenced will greatly influence the final polymer properties.

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