Journal of Thermal Analysis and Calorimetry, Vol. 83 (2006) 2, 355–359

KINETIC STUDY OF POLYURETHANES FORMATION BY USING DIFFERENTIAL SCANNING CALORIMETRY

W. Sultan[1] *and J.-P. Busnel*[2*]

[1]Department of Chemistry and Chemical Technology, CST, Al-Quds University, PO Box 20002 , Jerusalem
[2]Polymčres, Colloďdes, Interfaces, UMR CNRS, Faculté des Sciences, Université du Maine, 72085 Le Mans Cedex 9, France

Kinetics of polyurethane formation between several polyols and isocyanates with dibutyltin dilaurate (DBTDL) as the curing catalyst, were studied in the bulk state by differential scanning calorimetry (DSC) using an improved method of interpretation. The molar enthalpy of urethane formation from secondary hydroxyl groups and aliphatic isocyanates is 72±3 kJ mol^{-1} and for aromatic isocyanates it is 55±2 kJ mol^{-1}. In the case of a single second order reaction for aliphatic isocyanates reaction, activation energy is 70±5 kJ mol^{-1} with oxypropylated polyols and 50±3 kJ mol^{-1} with Castor oil. For aromatic isocyanates and oxypropylated polyols the activation energy is higher around 77 kJ mol^{-1}.

In the case of two parallel reactions (situation for IPDI and TDI 2–4) best fits are observed considering two different activation energies.

Keywords: *dibutyltin dilaurate, DSC, isocyanate, kinetics, polyol, polyurethane*

Introduction

The study of polyurethane (PU) is of continuing interest because of its various applications in the forms of foams, elastomers, adhesives and coating [1, 2]. The simplest PU is formulated from hydroxyl prepolymers of various functionality and well defined diisocyanate. That can give either linear, branched or gelled systems.

But the isocyanate can also react with other reactive hydrogen groups especially water, so the final properties of the polymer will vary according to the reaction route taken.

The rate and the extent of polyurethane formation thoroughly affect the rheological and mechanical properties of the polymer formed [3, 4]. Therefore, knowledge of the kinetics of polyurethane allows proper planning and controlling of the polymerization process as well as the prediction of polyurethane structure [5]. The kinetics data must be known in order to prepare PU polymers with the most convenient properties and with potential to produce final product with the most attractive physical properties.

The simplest way to obtain kinetic data is isothermal experiments in solution and direct titration of the remaining active NCO groups [4–6].

Quantitative IR gives also interesting results especially with the improvement of FTIR [7, 8]. The intensity of NCO stretching band at 4.38 μm is convenient for quantitative measurement of NCO concentration after proper calibration. But that method is only efficient for isothermal and slow reaction conditions.

Thermoanalytical techniques, especially DSC have been extensively employed to study the cure reaction of polymers [9, 10]. Assuming some approximations, the use of a constant heating rate allows extracting a complete set of kinetic and thermodynamic information in a reduced time. Direct integration of the exotherm of any sample of known initial composition allows to determine the molar enthalpy for kinetic parameters, various methods have been developed. The first method involves analysis of the exotherm at one heating rate. It is particularly successful for first order reactions. More refined methods compare the results at different heating rates and use integrated expressions of the kinetic scheme to extract the parameters: order of reaction, reaction rate and activation energy. They always suppose that the system is at a stoichiometric ratio. In some cases the key experimental parameter is the peak exotherm temperature but the more complete studies use the fact that surface of exotherm at a given time, gives the reaction extent. By this way various kinetic schemes have been tested including two simultaneous reactions and autocatalysed reactions with moderate success [11–14].

Modern computers allow handling easily large tables of thousands of lines, for that reason we consider that it is better to directly use differential expressions defining the kinetic scheme than to interpret the integrated expressions. That allows very direct comparison between experimental and theoretical data even for non stoichiometric systems.

---

[*] Author for correspondence: busnel@univ-lemans.fr

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

So, in this work, we have studied kinetics of the bulk reaction between several polyols and various isocyanates in the presence of homogeneous catalyst.

Results and discussion

Calibration

Temperature calibration was established from the onset of melting peak of water (0°C) and indium (156.6°C) used as standards with the same heating rate and cell geometry than for kinetic studies. The melting peak of pure indium is well suited to define the time constant of the cell. Analysis of the shape of the baseline return measured after the end of melting endotherm gives a time constant of 6 s. That implies broad exotherms like those studied in kinetic are not sensitive to such a small delay.

The cell constant which allows to calibrate heat flow values and to correct any technical drift is classically defined from the area of melting peak of indium. For the running conditions we use it as 1.07. To check the stability of that constant during temperature changes we have tested the shift between an empty cell and same cell loaded with a sapphire disk. We obtain the same value and a remarkable stability is observed with less than 1.5% change between 30 and 170°C (Fig. 1). A third run using same cell loaded with a known amount of polyol allows calculating the specific heats for that compounds. For the three oxypropylated polyols between ambient and 160°C, we obtain C_p=2.25±0.03 J g^{-1} $°C^{-1}$, for the refined Castor oil C_p=2.05±0.03 J g^{-1} $°C^{-1}$. An exothermic decomposition is observed for the three oxypropylated polyols at temperature higher than 170°C.

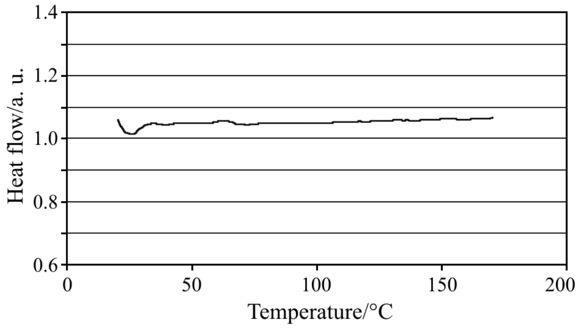

Fig. 1 DSC cell constant from sapphire calibration

Preliminary assumptions

In all systems, the main component is the polyol (more than 90% per mass). For that reason we consider that heat capacity and heat conductivity are constant during the reaction. In such conditions heat flow is correctly measured by the DSC apparatus and corresponds to the heat involved by the reaction rate:

$$\frac{dQ}{dt}=\frac{dn}{dt}\Delta H_{mol}$$

where n the number of moles of urethane and ΔH_{mol} the molar enthalpy of the reaction.

As the study concerns a temperature range of less than 100 K, we consider ΔH_{mol} as constant.

Interpretation of single reaction systems

In that case, we consider situations where there is only one category of hydroxyl groups, one category of isocyanate groups, a stoichiometric ratio (NCO/OH) lower than one and a homogeneous catalysis.

For such systems it is well established that the reaction is second order, with no side reactions, and the reaction rate is proportional to the catalyst concentration [1, 6, 7, 12]. The use of low stoichiometric ratio prevents to reach high viscosity which can slow up the reaction.

To extract reaction rates and activation energy from experimental exotherms we have used a spreadsheet build with one line per second.

In one column, we copy the experimental data dQ/dt after baseline correction.

Let us call S_t the heat evolved from 0 to time t, and S_{tot} the total heat evolved at the end of the reaction.

That allows to calculate the urethane concentration at time t $x=[NCO]_0\ S_t/S_{tot}$.

Similarly the hydroxyl concentration is $b=[OH]_0-x$ and the isocyanate concentration is $a=[NCO]_0-x$ (all concentrations are expressed in mol L^{-1}, reaction rates in mol L^{-1} s^{-1}).

The kinetic scheme is OH+NCO→U

and the reaction rate $v=\frac{dx}{dt}=k'ab$.

Let us note Vol the total volume of the sample,

$$v=\frac{dx}{dt}=\frac{1}{Vol}\frac{dn}{dt}=\frac{1}{Vol\,\Delta H_{mol}}\frac{dQ}{dT}$$

That allows to extract values of $k'$for any time and so for any temperature T

$$k'=\frac{v}{ab}$$

Then lnk' and $1/T$ are calculated to give access to the Arrhenius plot $\ln k'=f(1/T)$ with slope of $-E_a/R$, E_a being the activation energy of the reaction. The k' value is a second order rate coefficient including the efficiency of the catalyst. To check for the role of catalyst we have also calculated a third order rate coefficient value $k=k'/[Cat]$.

Table 1 Single reaction results

Polyol	Isocyanate	$[OH]_0$/ mol L^{-1}	$[NCO]_0$/ mol L^{-1}	[Cat]/ mol L^{-1}	ΔH_{mol} kJ mol^{-1}	k'_{298}/ L mol^{-1} s^{-1}	k_{298}/ L^2 mol^{-2} s^{-1}	E_a kJ mol^{-1}
PPG 1000	HMDI	1.86	0.45	1.12E-04	72	7.7E-06	6.9E-02	70
PPG 2000	HMDI	0.95	0.37	2.97E-04	70	2.9E-05	9.8E-02	65
Arcoll 1070	HMDI	3.95	0.45	2.99E-04	69	2.4E-05	8.1E-02	68
Arcoll 1070	HMDI	3.95	0.45	1.02E-04	71	9.0E-06	8.9E-02	67
Desmophen 1150	HMDI	3.35	0.37	1.00E-04	73	1.4E-05	1.4E-01	50
Desmophen 1150	HMDI	3.39	0.24	1.05E-04	75	1.3E-05	1.2E-01	50
PPG 1000	nOI	1.87	0.21	1.17E-04	74	6.4E-06	5.4E-02	75
PPG 1000	pTI	1.88	0.21	3.21E-05	55	9.3E-06	2.9E-01	79
PPG 1000	MDI	1.89	0.19	4.05E-05	56	1.4E-05	3.6E-01	75
PPG 1000	TDI 2–4	1.89	0.31	9.77E-05	58			
PPG 2000	IPDI	0.94	0.34	1.07E-04	74			

Results are summarized in Table 1 and an example of Arrhenius plot is given in Fig. 2. We observe an excellent fit for the main part of the exotherm corresponding to more than 70% of the surface. It remains small discrepancies due to imperfect baseline definition. Table 1 indicates that the molar enthalpy of urethane formation from secondary hydroxyl groups and aliphatic isocyanates is 72±3 kJ mol^{-1} and for aromatic isocyanates it is 55±2 kJ mol^{-1}. From those results, we can consider that, for TDI and IPDI, the two different isocyanate groups have equal molar enthalpy of reaction.

For aliphatic isocyanates reactions, activation energy is 70±5 kJ mol^{-1} with oxypropylated polyols and 50±3 kJ mol^{-1} with Castor oil. For aromatic isocyanates and oxypropylated polyols the activation energy is 77±5 kJ mol^{-1}.

At temperature lower than 298 K, reaction rates are sufficiently slow to allow efficient mixing during a few minutes without significant extent of reaction. To check precisely that point, let us note Δx the urethane concentration after a time of mixing Δt.

$$\frac{\Delta x}{[\mathrm{NCO}]_0}=k'[\mathrm{OH}]_0\Delta t$$

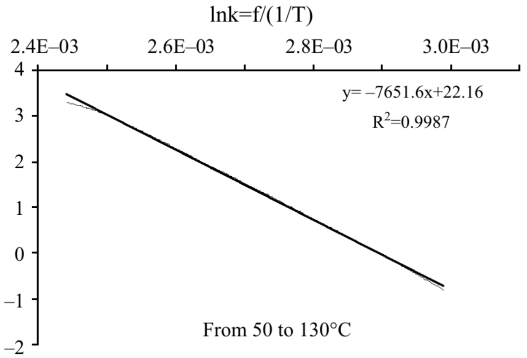

Fig. 2 Arrhenius plot for system PPG2000/HMDI r=0.39

In the worse situation, for a mixing time of four minutes $\frac{\Delta x}{[\mathrm{NCO}]_0}$ remains lower than 2.5%.

These results confirm the higher absolute reactivity of aromatic isocyanates compared to aliphatic ones and it appears that hydroxyl groups from Castor oil are more reactive at ambient temperature than those of oxypropylated polyols. But that difference vanishes at higher temperature as the activation energy is lower for Castor oil.

Third order rate coefficient at 298 K and activation energy values allow easy calculation of the reaction rate at any temperature and catalyst concentration and so allow easy prediction of the reaction extent at any time for a realistic system on isothermal conditions.

Interpretation of two parallel reactions

Isothermal kinetic studies allow extracting results for such systems only in the case of important difference of reactivity [8]. Some results have also been obtained by determination of the composition of reaction mixtures between a diisocyanate and a simple diol [15] or monoalcohol [16]. In such cases stoichiometric ratio lower than one are used (typically r =0.5) and, at the end of reaction, the distribution of non reacted hydroxyl, monourethane and diurethane is sensitive to the ratio of reactivity of the two for different isocyanate groups. But that method does not give absolute values of reactivities.

Theoretically the problem of reaction of a diisocyanate with non equivalent groups is a complex one. Difference of reactivities can be intrinsic or by substitution or both.

In the first case we observe simply two parallel reactions:

$$\mathrm{A1+OH \rightarrow U1}$$

$$A2+OH \rightarrow U2$$

Each diisocyanate bears one group A1 and one group A2.

We can assume that each reaction has its own reaction rate, activation energy and molar enthalpy.

Such a situation corresponds to IPDI and TDI 2–4 if we neglect the substitution effects.

For substitution effect we observe two consecutive reactions: the scheme is:

$$A\text{---}A+OH \rightarrow U\text{---}A$$

$$U\text{---}A+OH \rightarrow U2$$

That can be observed for symmetrical molecules like 2–6 TDI.

The complete scheme corresponds to four reactions: There are two different isocyanate groups and, once a first group has reacted, the reactivity of second group is changed

$$A1\text{—}A2+OH \rightarrow U1\text{—}A2$$

$$A1\text{—}A2+OH \rightarrow A1\text{—}U2$$

$$U1\text{—}A2+OH \rightarrow U1\text{—}U2$$

$$A1\text{—}U2+OH \rightarrow U1\text{—}U2$$

In the present work we have used the differential approach which was still proposed and there is no difficulty to treat any situation. But handling a large number of adjustable parameters doesn't allow obtaining safe conclusions. Pure substitution effect is rarely observed for usual diisocyanates, for that reason we have limited our study to the first case: two parallel reactions.

The basic idea is to build the shape of a theoretical exotherm corresponding to a complete set of parameters and to compare that exotherm to the experimental one. Interactive adjustments of the parameters allow finding the convenient set corresponding to the real system.

These parameters are molar enthalpies, reaction rates at a given temperature and activation energies for both reactions.

We build a new spreadsheet with one line per second and as many columns as necessary to define the situation of the system and the differential changes of it during one second (or any other time increment).

At time zero we know concentrations of each reactive group, [A1], [A2], [OH], the temperature and the heating rate.

For each line that allows to calculate the two second order rate coefficient k'_1 and k'_2, the two reaction extents and the quantities $dA1=k'_1\,[A1]\,[OH]$, $dA2=k'_2\,[A2]\,[OH]$, $dOH=dA1+dA2$ and the quantity $Y=Q/\mathrm{Vol}=\Delta H1\cdot dA1+\Delta H2\cdot dA2$, which is proportional to the heat flow.

Those values of Y are then normalized to allow easier comparison with the experimental results.

From one line to the other, all the active parameters are refreshed.

The exported experimental data are handled to run the baseline correction and then to normalize it.

Finally an interactive graph is observed which allows us to adjust parameters until superposition of

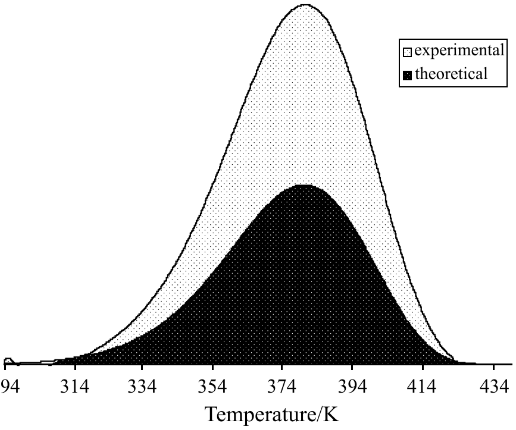

Fig. 3 Exotherms for system PPG2000/HMDI $r = 0.39$

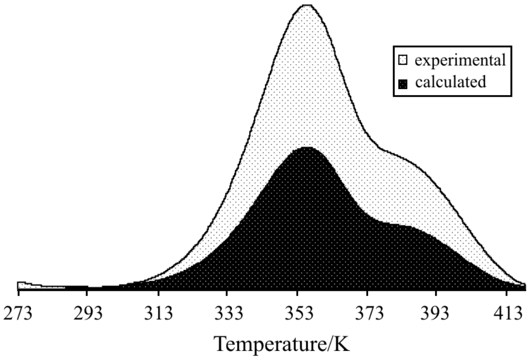

Fig. 4 Exotherms for system Arcol1070/IPDI $r = 0.12$

Table 2 Two parallel reactions results

Polyol	Isocyanate	$[NCO]_0/[OH]_0$	[Cat]/ mol L^{-1}	$k'_{1\,(298\,K)}$/ L mol^{-1} s^{-1}	E_{a1}/ kJ mol^{-1}	$k'_{2\,(298\,K)}$/ L mol^{-1} s^{-1}	E_{a2}/ kJ mol^{-1}
PPG 1000	IPDI	0.22	3.4E-04	4.0E-05	85	2.0E-05	60
Acrol 1070	IPDI	0.12	5.1E-04	3.0E-05	87	2.7E-05	60
Acrol 1070	TDI 2–4	0.10	0.8E-05	1.5E-05	85	1.1E-05	61
Acrol 1070	TDI 2–4	0.10	0.5E-05	3.2E-05	75	7.0E-06	48

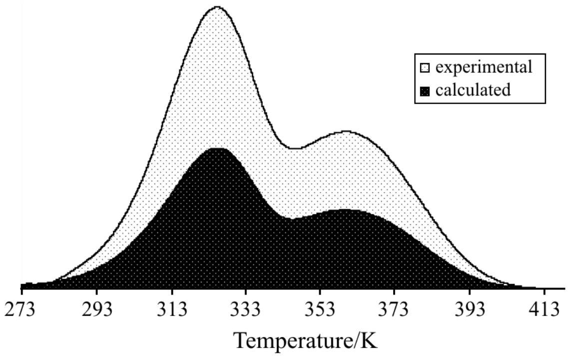

Fig. 5 Exotherms for system Arcol1070/TDI 2–4 r= 0.10

both exotherms. In the situation of only one reaction, the best fit is obtained for the same values of reaction rate and activation energy than using the previous method (Fig. 3). For experiments using IPDI or TDI 2–4 the curves have bimodal shapes, clearly indicating a difference of reactivity between the two isocyanate groups. (Table 2, Figs 4, 5).

The best fit is obtained when giving a higher activation energy to the more reactive isocyanate group so the difference of reactivity is enhanced for higher temperatures.

Conclusions

DSC monitoring of the polyurethane formation from mixtures of polyols and diisocyanates allows to extract efficiently a complete set of kinetic parameters in a short time by using a spreadsheet which takes into account the differential changes of the system along time.

The main difficulty is to have sufficiently slow reaction at the temperature of preliminary mixing of the ingredients. Proper adjustment of catalyst concentration allows to fulfill that condition.

The higher reactivity of aromatic isocyanates compared with aliphatic ones clearly appears.

In the case of IPDI and TDI 2–4, best fits are obtained for two different activation energies. That implies that in both cases, the difference of reactivity between the two isocyanate groups increases on increasing temperature.

That method can be used efficiently to check any particular system in order to predict best temperature and time of reaction. That is also interesting when testing a new catalyst.

Acknowledgements

The authors thankfully acknowledge TEMPUS program for financial support by an individual mobility grant and M. Gérard Guevelou from Polymčres, Colloďdes, Interfaces laboratory for his kind technical support.

References

1 M. Szycher, Szycher’s Handbook of Polyurethanes, CRC Press (1999).
2 Z. Wirpsza, Polyurethanes, Ellis Horwood Ltd. (1993).
3 R. M. Muthiah, V. N. Krishnamurthy and B. R. Gupta, J. Appl. Polym. Sci., 44 (1992) 2043.
4 Y. Cui, L. Hong, X. Wang and X. Tang, J. Appl. Polym. Sci., 89 (2003) 2708.
5 C. M. Thompson, J. Polym. Sci.: Part A 28 (1990) 333.
6 S. Ajithkumar, S. S. Kansara and N. K. Patel, Eur. Polym. J., 34 (1998) 1273.
7 D. Kincal and S. Özkar, J. Appl. Polym. Sci., 66 (1997) 1979.
8 M. A. Semsarzadeh and A. H. Navarchian, J. Polym. Engineering, 23 (2003) 225.
9 E. A. Turi, Thermal Characterization of Polymeric Material, Acad. Press (1981).
10 X. Ramis, J. M. Salla, A. Cadenato and M. Morancho, J. Therm. Anal. Cal., 72 (2003) 707.
11 K. B. Catherine, K. Krishnan and K. N. Ninan, J. Therm. Anal. Cal., 59 (2000) 93.
12 F. Hernandez-Sanchez and R. Vera-Graziano, J. Appl. Polym. Sci., 46 (1992) 571.
13 C. Korah Bina, K. G. Kannan and K. N. Kannan, J. Therm. Anal. Cal., 78 (2004) 753.
14 J. M. E. Rodrigues, M. R. Pereira, A. G. de Souza, M. L. Carvalho, A. A. Dantas Neto, T. N. C. Dantas and J. L. C. Fonseca, Thermochim. Acta, 427 (2005) 31.
15 P. Krol, J. Appl. Polym. Sci., 69 (1998) 169.
16 P. Krol and B. Pilch-Pitera, Eu. Polym. J., 37 (2001) 251.

Received: March 20, 2005
Accepted: September 12, 2005

DOI: 10.1007/s10973-005-7026-8