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INFLUENCE OF THE MACRODIOL CHAIN LENGTH ON THE KINETICS OF LINEAR NON-SEGMENTED AND SEGMENTED POLYURETHANES

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ABSTRACT

The aim of this study is to determine the influence of the macrodiol chain length on the kinetics of polyurethane formation of segmented and non-segmented polyurethanes. Differential thermal analysis and the adiabatic reactor method were used to study uncatalysed and catalysed systems, respectively. The kinetic results are discussed with reference to the Arrhenius equation. The helical structure as well as the domain formation have enabled us to explain the kinetic behaviour of the carbamate formation reaction.

INTRODUCTION

Recently, the bulk polymerization of polyurethanes has attracted increasing interest [1–9] because this polymer is usually processed in this state. The monitoring of bulk reactions can be achieved by differential calorimetry, the adiabatic reactor method, infrared spectroscopy, NCO titration and by other techniques. The first two methods are used in this research.

The main aim of this work is to determine the influence of the macrodiol chain length on the reaction kinetics of linear non-segmented and segmented polyurethane. In order to fulfil this objective, polyethylene oxides of different molecular weights have been used. This polymer is characterized by a distorted (7/2) helix, close to the TTG repeating sequence of the uniform model [10]. Kusagani et al. [11], using the packing energy minimization method to account for intermolecular interactions, found a structural model very similar to the structure determined by X-ray analysis, and concluded that the distorted helix is, thus, a consequence of the supposed intermolecular forces.

This helical structure is, moreover, responsible for the existence of a positive charge distribution along the ether chain. In order to account for the structural differences, we have studied the influence of the chain length of linear polyurethanes.

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Segmented polyurethanes show a statistical hard segment distribution which is controlled by the molar ratio, w, of macrodiol to polyisocyanate [12]. This statistical distribution gives rise to diffuse domain boundaries (no chain folding takes place), being the segregated hard segment extended and penetrating the soft matrix in a way which depends on the hard segment length. Domain stability is related to crosslinking stability which depends on the chemical nature of the chain extenders, the hard segment length, the domain size and the nature of the soft segments (these do not contribute directly to the domains but influence the domain formation rate).

In this study, 1,4-butanediol has been used as the chain extender. This is one of the most widely employed chain extenders. The good thermal and mechanical properties associated with 1,4-butanediol-segmented polyurethanes is related to the existence of transverse crosslinking which allows for planar co-operation.

EXPERIMENTAL

The reagents, used as received, were methylene diphenyl di-isocyanate (Merck: a mixture of di- and tri-isocyanate, equivalent weight (ASTM D-1638-74) being 137.9 (g equiv.)$^{-1}$) polyethylene glycols (Merck: molecular weights 200 (PEG200), 400 (PEG400) and 600 (PEG600) g mol^{-1}) and 1,4-butanediol (Merck). The catalyst DBTDL (Ciba–Geigy) was provided by ICOA S.A.

Differential thermal analysis (DTA)

The uncatalysed reaction kinetics were followed, recording the temperature increment evolved during the exotherm. The calorimetric system used was a computerized Mettler TA2000. The DTA system was calibrated weekly with indium. Because of the proportional character of the reaction rate with respect to the enthalpy change, this analytical method allows us to determine the kinetic features of the different systems. Equation (1) illustrates this proportional character

$$\mathrm{d}n/\mathrm{d}t = (\mathrm{d}\Delta H/\mathrm{d}t)\ \Delta H_{\mathrm{sp}} \tag{1}$$

where n is the number of reactive molecules, ΔH is the enthalpy change and ΔH_{sp} is the reaction enthalpy, i.e. the total exotherm area, the experimental value of which, in these systems, lies in the energy range 37.62–47.24 kJ equiv.$^{-1}$ [4,13].

The conversion-time function can be obtained from the exotherm time-dependent partial area

$$P = (C_0 - C)/C_0 = \Delta H(t)/\Delta H_{\mathrm{sp}} \tag{2}$$

The reaction rate constant has been determined by means of the integration method

$$1/(x-1)\left[(1-P)^{(1-x)}-1\right]=KC_0^{(x-1)}t \quad (3)$$

The overall reaction order, x, has been calculated by varying its value between 0 and 4 until the values of the left side of eqn. (3) fit a straight line as a function of time. Activation energy values have been obtained using the well-known Arrhenius equation.

The reactive mixture was prepared by weighing the equivalent amounts of raw materials in a crystal vessel. After stirring the mixture, a certain amount (10–15 mg) was transfered to the DTA sample pan. The whole procedure was carefully time-controlled in order to reproduce the conditions for each system.

The adiabatic reactor method

The reaction kinetics were followed by monitoring the adiabatic temperature change as a function of time. This method has been reported to be the most convenient for fast bulk-polymerizing systems [9]. The data analysis was carried out using [9]

$$\ln K=\ln\left\{(\mathrm{d}T/\mathrm{d}t)/\left\{\Delta T_{\mathrm{ad}}\left[1-(T-T_0)/\Delta T_{\mathrm{ad}}\right]^n\right\}\right\}=\ln A-E_{\mathrm{a}}/RT_{\mathrm{exp}} \quad (4)$$

where K is the rate constant, n is the reaction order, T_{exp} is the experimental temperature, T is the adiabatic temperature (obtained by correcting the experimental temperature using the heat lost factor), $\Delta T_{\mathrm{ad}}=(-\Delta H)/C_{\mathrm{p}}$, $-\Delta H$ being the heat evolved per unit mass and C_{p} the specific heat (considered herein as constants although this is not a compulsory condition), T_0 is the room temperature, A is the Arrhenius pre-exponential factor and E_{a} is the reaction activation energy.

The reactor was a glass tube 115 mm long and 23 mm in diameter insulated with closed-cell polystyrene foam (Dow Chemical) in order to achieve adiabatic conditions. An iron–constantan thermocouple was used to measure the adiabatic temperature rise which was monitored with an IBM computer.

The stoichiometric amounts of the heated components were poured into the reactor together with the catalytic system, and the whole was stirred using a two-propeller motor-mixer.

RESULTS AND DISCUSSION

The aim of this work was to assess the influence of macrodiol chain length on the kinetics of non-segmented and segmented linear polyurethanes. This aim has been achieved by studying the kinetic behaviour of a set of polyurethanes characterized by the presence or absence of 1,4-butanediol and polyethylene glycols with molecular weights between 200 and 600 g mol^{-1}, in which range polyethylene glycol is a liquid. The uncatalysed reactions have been monotored using a computerized DTA system whilst the catalysed reactions was followed using the adiabatic reactor method.

For simplicity, we have considered the NCO reactivity to be independent of its position within the molecule and of the reaction, or not, of the other reactive groups belonging to the same molecule [14,15].

Uncatalysed systems

Application of the integration method yields reaction orders ranging from 1.5 to 2. As values in the literature [2,4,16] fluctuate between 1 and 2, we have considered 2, which corresponds to the Baker–Holdsworth mechanism [17], to be the appropiate order for all the systems. The second-order rate constants for the uncatalysed unextended linear polyurethane are shown in Table 1.

As can be seen in this table, the rate constants for the four systems lie in a very narrow range, with a marked similarity between the systems containing 1,4-butanediol and PEG400, and between the systems with PEG200 and PEG600. These differences in the rate constants with increasing molecular weight can be related to the structural features pointed out at the beginning of this paper; 1,4-butanediol has a zig-zag structure whilst PEG200, PEG400 and PEG600 have helical conformations with a 1, 3 and 4 helix pitch, respectively. Due to the distorted character of the helix, together with the fact that the average for PEG200 is only one helix pitch, we assume that this macrodiol has an almost zig-zag conformation. These structural differences allow us to suggest a somewhat different type of activated complex formation within the same mechanism: the presence of a small positive charge distribution, due to the helical structure, gives rise to a less energetic activated complex in which there are dipole interactions between the positive PEG charge distribution and the negative one associated with the aromatic

TABLE 1

Kinetic parameters of the uncatalysed-unextended systems

System	K (l $equiv.^{-1}$ s^{-1}) at T_r (K) =				E_a (kJ mol^{-1})
	323	333	343	353	
MDI/BD	1.03	1.68	2.82	4.40	46.45
MDI/PEG200	0.85	1.43	2.50	3.90	48.71
MDI/PEG400	0.98	1.55	2.72	4.11	45.34
MDI/PEG600	0.85	1.43	2.50	3.95	49.07

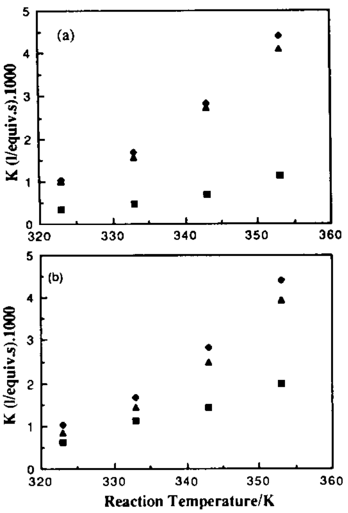

Fig. 1. Plots of the second-order rate constants against isothermal reaction temperature. ■, Uncatalysed-extended MDI/BD/PEG400 system (Fig. 1a); ■, uncatalysed-extended MDI/BD/PEG600 system (Fig. 1b); ◆, uncatalysed MDI/BD system; ▲, uncatalysed MDI/macrodiol system.

resonance structures corresponding to the MDI molecule. The differences found within the members of the same structural groups could arise from diffusion phenomena such as chain transport to the reactive centres. The activation energy values seem to corroborate this as they reflect the structure and the chain length.

Segmented polyurethane shows a hard segment distribution with a mean value, p, of the MDI blocks given by [12]

$$p = 1 + 1/w \tag{5}$$

where w is the molar ratio of macrodiol to MDI. This molar ratio, in our case, is 0.68, the equivalent ratio MDI/BD/PEG being 2/1/1. Thus, in our systems, hard segment distribution of MDI blocks is found to have a mean value of 3.

The kinetic behaviour associated with the two segmented systems investigated herein (MDI/BD/PEG400 and MDI/BD/PEG600) is shown in Fig. 1 where the reaction constants have been plotted as a function of temperature. From this figure it is striking that: the reaction constants for both segmented systems are much lower than for the non-segmented ones; and the reaction proceeds much faster for the system MDI/BD/PEG600 than for MDI/BD/PEG400.

The first feature can be explained with reference to the domain formation trend characteristic of these types of systems. The presence of 1,4-butanediol brings about transverse crosslinking and multiphase formation, resulting in an increased macroscopic viscosity which slows down the reaction rates. The second feature may be explained by the different rate constants found for the binary systems. In the tertiary system MDI/BD/PEG400, the two diol molecules show very similar reaction rates (see Table 1), there being a possible competitive process between the macrodiol and chain extender, which slows down the overall tertiary system rate constant. This is not the case for the system MDI/BD/PEG600, where the very different reaction rates between the diols enables the chain extender to react before the macrodiol; thus, the reaction rate for this system is larger than for the other chain-extended system. In the MDI/BD/PEG600 system, the mean value of the MDI blocks within the hard segment probably changes as a function of conversion, being larger for low reaction times and becoming lower as conversion proceeds.

In addition to the above observations, the Arrhenius activation energies determined are lower than those found for the non-segmented systems: 38.22 (MDI/BD/PEG400) and 35.64 (MDI/BD/PEG600) kJ mol^{-1}. The presence of a unique exotherm confirms the competitive character of the blended diols from a kinetic standpoint.

Catalysed systems

In order to compare the kinetic parameters in uncatalysed and catalysed polyurethane reactions, the study of three unextended systems catalysed with dibutyltindilaurate has been studied using the adiabatic reactor method. These systems were MDI/PEG200, MDI/PEG400 and MDI/PEG600.

The semi-reaction times as a function of catalyst concentration were plotted for the three systems (Fig. 2). It is clear from this figure that the systems MDI/PEG200 and MDI/PEG600 display very similar semi-reac-

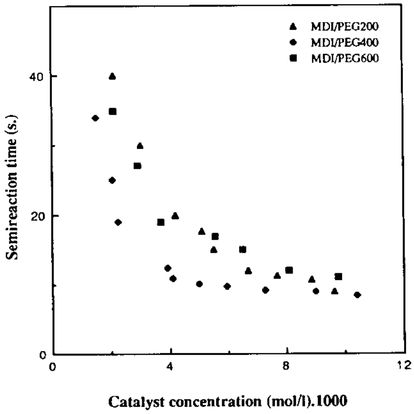

Fig. 2. Plot of semi-reaction times as a function of catalyst concentration obtained by the adiabatic reactor method.

tion values, whilst the system containing PEG400 shows much lower semi-reaction times, especially at low catalyst concentrations.

Application of eqn. (4) enables the determination of reaction orders and activation energies. As in the case of uncatalysed reactions, the overall reaction order falls between 1.5 and 2, which is in good agreement with the literature [3,5,9]. Once the reaction order has been calculated, the activation energy determination becomes possible. The activation energy values associated with the macrodiol PEG200 are higher than the values corresponding to the macrodiols PEG400 and PEG600. These results suggest a somewhat different reaction mechanism dependent on the structure of the polyethylene oxides, as has been pointed out elsewhere within this paper.

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