Competition of aminolysis and alcoholysis in nucleophilic cleavage of a model compound for polysiloxane networks

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Abstract

Base-catalysed aminolysis and ethanolysis of room temperature vulcanised poly(dimethylsiloxane) networks were studied with the aid of a model compound, tetrakis(trimethylsiloxy)-silane. Ethanol and ethylamine were used as nucleophilic reagents. The nucleophilicities of the reagents were enhanced by addition of potassium hydroxide.

Kinetic models for the aminolysis and alcoholysis reactions at the initial stage were developed. The models reasonably predict the experimental data. Initial rate analysis was employed to determine the parameters of aminolysis and ethanolysis rate expressions. The overall activation energy of the aminolysis reaction is 14 kJ/mol. The initial rate of aminolysis was faster than that of ethanolysis. However, aminolysis reached equilibrium much faster than ethanolysis. When competition occurred in the reaction system, the aminolysis reaction dominates nucleophilic substitution at the initial stage and is followed by ethanolysis in a subsequent step.

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Keywords: Aminolysis; Alcoholysis; Base catalyst; Model compound; Poly(dimethylsiloxane) network

1. Introduction

Room temperature vulcanised poly(dimethylsiloxane) (PDMS) networks can be broken down by amines at ambient temperature to form linear polymers [1,2]. The aminolysis reaction can be enhanced with the aid of a strong base such as potassium hydroxide or sodium ethylate and the dissolution time of the networks can hence be reduced from days to hours [3–5]. It is believed that the splitting selectively prefers tetra-functional siloxane units rather than di-functional ones in the RTV PDMS networks due to the greater electrophilicity of silicon which is enhanced by the presence of two additional oxygen substituents. Potassium hydroxide could only sparingly be dissolved in amines which increases the degree of difficulty in a dynamic study of the splitting reaction. Internal diffusion resistance should be significant in the PDMS networks when an ionic compound such as KOH is employed as a catalyst. In a previous work, the rate of the aminolysis reaction of PDMS networks at ambient temperature was significantly enhanced by adding ethanol to the KOH/DEA solution system and the process time was reduced to the order of 10 min [6]. The results were attributed to the complete dissolution of potassium hydroxide and the fact that heterogeneous interfacial diffusion resistance was not present. A possible mechanism was proposed to explain the enhancing effects of the catalyst and the role of ethanol as the second nucleophile. With internal diffusion limitation in the crosslinked PDMS matrix, a rational kinetic study on the intrinsic reactions cannot be achieved without the aid of a model compound. Organoxysilanes are extensively used as object

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compounds in the studies of the cleavage reaction of siloxane bonding. An excellent review of the literature can be found in a text by Voronkov and Basenk which indicates that the cleavage reaction does not occur when organoxysilanes are treated with amines and that the alcoholysis of organoxysilanes can be carried out in the presence of acids and bases [7]. Although information on the kinetics of alcoholysis of organoxysilanes exists in limited form, the molecular structure of organoxysilane is somewhat different to the crosslinked structure of cured PDMS, and thus cannot be employed as a model compound in the kinetic study of the competition of aminolysis and alcoholysis reactions of PDMS networks.

In the present work, base catalyst enhanced aminolysis and ethanolysis reactions of room temperature vulcanised PDMS networks were investigated with the aid of a model compound, tetrakis(trimethylsiloxy)silane (M_4Q). A mechanism was proposed to elucidate the enhancing effect of the catalyst and the rate laws of both reactions were developed. The parameters of the rate expressions were determined by initial rate analysis.

2. Experimental

The reactions were carried out in glass flasks at low temperature. M_4Q (97%, Riedel-dehaen), ethanol (99%, Riedel-dehaen), ethylamine (>99%, ACROS) and *p*-xylene (99%, ACROS) were kept in a refrigerator before use. Proper amounts of ethylamine, xylene and potassium hydroxide were mixed in a sealed flask. The flask was mixed by magnetic stirrer and placed in a constant low temperature water bath at 5 °C. M_4Q was also weighed and added to another flask in the water bath. After temperature equilibrium was reached, M_4Q was added to the flask with well-mixed ethylamine solution and timing was started. The initial concentrations of M_4Q, ethylamine and KOH were 0.64, 2.46 and 0.005 M, respectively. After the reaction started, samples were removed using a syringe and injected into a GC to analyse the product distributions. The first two samples were taken 5 and 20 min after the reaction started. Samples were then taken every 10 min. Because its boiling point deviated from those of other species and its inertness in these reactions, xylene was used as the internal standard in the GC analysis. Response factors for each compound relative to xylene were determined.

3. Results and discussion

The aminolysis and alcoholysis reactions were conducted at low temperature (5 °C) for two reasons: one is to avoid ethylamine evaporation as the aminolysis reaction proceeds and the other is to reduce the reaction

rates for greater ease of measurement. The experimental results of aminolysis reaction are shown in Figs 1–3. The concentrations of reactants, M_4Q and ethylamine, decrease as the reaction time elapses and level off after 30 min which indicates that the reaction is reversible. The concentration of singly substituted product increases with time as shown in Fig. 3. The successive nucleophilic cleavage reactions were significant as evidenced by the low formation rate of singly substituted product. Products with high molecular weights via sol–gel reaction could not be detected by gas chromatography.

Figs. 4 and 5 present the experimental results of alcoholysis reaction system. The data from competitive reaction runs involving both nucleophilic reagents are also shown in Fig. 4. In the period of reactions conducted, the reactant concentrations kept decreasing and there is no sign of the alcoholysis reaction reaching equilibrium. The reverse reaction of alcoholysis is clearly slower than that of aminolysis since the equilibrium state cannot be reached within the time period. Thus the aminolysis reaction rate is much faster than the alcoholysis reaction rate. It is believed that ethylamine is a more effective nucleophilic reagent than ethanol. However, both reagents cannot be effective nucleophiles unless they are catalysed by KOH and form ion pairs as postulated in a previous paper [6]. The plus effect was not obtained when total nucleophile concentration was doubled in the competition reaction system. The initial concentration of KOH is the same in all runs. KOH pairing competition between the two nucleophiles could be the main reason for the reduction of the additive effect. The pairing of ethanol and KOH is postulated to be faster than amine and KOH, and affects the subsequent nucleophilic cleavage reaction. The displacement of amino group from silicon by ethoxy group was observed in the previous work [6]. When the two reactions compete, the aminolysis reaction dominates the substitution reaction in the initial stages and is followed by ethanolysis at a later stage as evidenced by the non-stop reaction trend in Fig. 4.

Based on the observations of the reactions, a possible mechanism for the aminolysis reaction is postulated in the following scheme:
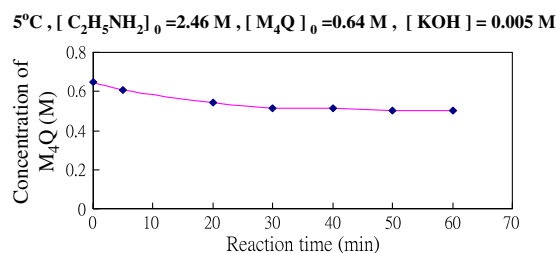
5°C , $[C_2H_5NH_2]_0$ =2.46 M , $[M_4Q]_0$ =0.64 M , $[KOH]$ = 0.005 M

Fig. 1. Concentration of M_4Q versus reaction time in the aminolysis reaction.