New experimental analytical technique for gelling system kinetics*

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A new experimental analytic technqiue which may be used to monitor the progress of reaction in a gelling system up to and beyond the gel point is presented with an attempt to use the data obtained therefrom for kinetic analysis of a random non-linear polymerization involving a difunctional acid chloride, sebacoyl chloride, and a trifunctional alcohol, LHT240 [a poly(propylene oxide) hexanetriol], in the presence or absence of an ethereal solvent, diglyme. For the system studied, reactions were found to accord with simple second order kinetics, devoid of buried group effect, and are explained by means of a simple mechanism in contrast to some earlier literature reports of complex order kinetics for similar systems.

INTRODUCTION

The reaction between an alcohol and an acyl chloride can be represented by the equation

$$ROH + R'COCl \rightarrow R'CO \cdot OR + HCl$$
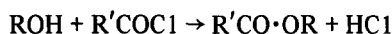
In general the mechanism of the reaction (mono- or polymeric) has been found to be rather complex owing to[1-4]:

(a) the association of alcohols through their hydroxyl groups: this affects the accessibility of the hydroxyl groups for reaction;

(b) the effect of the solvent: although chemically inert, the solvent may take part in the formation of a transition state or may be assocated with the alcohol;

(c) the possibility of a dual mechanism for one reaction, the predominant mechanism being a function of the polarity of the reaction medium;

(d) the effect of buried groups within the network, making reaction increasingly difficult as the system approaches gelation;

(e) the non-specificity or non-integral nature of the order of the reaction in relation to concentration of the systems studied.

The fact that the reaction mixture in a gelling system loses its fluidity after gelation has probably been the main obstacle to the study of post-gelation kinetics in acyl chloride–alcohol systems. In this paper, an analytical technique to monitor accurately the progress of reaction in such systems is presented and a kinetic analysis of acyl chloride–alcohol non-linear polymerization is proposed.

EXPERIMENTAL

Materials, techniques and equipment

The gelling system studied is a non-linear random polymerization involving stoichiometric quantities of a poly(propylene oxide) hexanetriol, LHT240, (T), and one of two difunctional acyl chlorides, sebacoyl chloride (SC) and adipoyl chloride, (AC), in the presence or absence of an ethereal solvent, diglyme, and covering the widest range of practically possible dilution at 300K. Experiments to monitor the progress of reaction up to and beyond the gel point were based on monitoring the extent of reaction with respect to acyl chloride.

T was a poly(propylene oxide) adduct of 1,2,6-hexanetriol, with a narrow, almost Poisson, molecular weight distribution, supplied by Union Carbide (UK) Ltd, which has been shown[5] to possess equally reactive functional groups and hence to be suitable for network formation studies. It can be represented by the structural formula:

$$
\begin{array}{l}
\quad\quad\quad\quad\quad\quad\quad CH_3 \\
\quad\quad\quad\quad\quad\quad\quad | \\
CH-(O-CH_2-CH)_{\bar{n}}-OH \\
| \\
CH-(O-CH_2-CH)_{\bar{n}}-OH \\
|\quad\quad\quad\quad\quad\quad\quad | \\
(CH_2)_3\quad\quad\quad\quad\quad CH_3 \\
| \\
CH_2-(O-CH_2-CH)_{\bar{n}}-OH \\
\quad\quad\quad\quad\quad\quad\quad | \\
\quad\quad\quad\quad\quad\quad\quad CH_3
\end{array}
$$
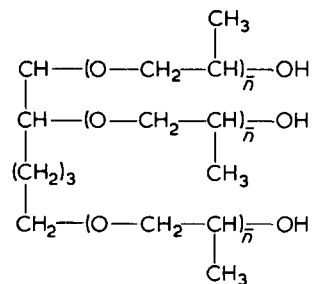
where $\bar{n}$ is the number-average degree of polymerization for each branch of the triol monomer. For T used in this study, purification was by means of the method described by Smith and Stepto[4], $\bar{n} = 3.3$, and number-average molecular weight, $M = 692.1 \pm 2$.

SC and AC were supplied by BDH. Each was purified by

Table 1 Purification data on acyl chlorides

Material	Method of analysis	Equivalent weight (EW) Experimental	Theory
SC	Acidimetry	120.08	119.54
	Chloride titrimetry	119.53	
AC	Acidimetry	91.58	91.52

redistillation at reduced pressure in an atmosphere of nitrogen in 3-necked 250 ml flask. The fractions of SC and AC which distilled in the temperature ranges $122°-124°C$ and $79°-81°C$ respectively at 0.08–0.09 torr were collected. The purification was carried out in 100 ml batches as larger quantities resulted in extensive decomposition in the distillation flask. The purity of the redistilled acid chloride was estimated by determining its equivalent weight, by means of one or both of the methods described by Smith and Stepto[4]. Results of the analyses are given in *Table 1*. The theoretical values of *EW* for the acid chlorides were used in the determination of the acid chloride content of reaction mixtures.

Laboratory grade diglyme was supplied by BDH. It was purified by redistillation in 2.5l portions over fused anhydrous calcium chloride and sodium metal in turn. The fraction which boiled in the range $160°-162°C$ gave a negative test for peroxides in 10% potassium iodine aqueous solution acidified with hydrochloric acid, and was used for the reaction systems studied.

Gelling polycondensation systems

Polycondensation reactions were carried out at 300 and 333K respectively in systems containing stoichiometric quantities of acyl chloride and triol in diglyme. The proportion of diglyme in the reaction mixture varied from 0 to 85% by wt. Known weights of triol and diglyme were placed in a tared multi-neck reaction vessel, in a water bath maintained at the required temperature with an accuracy of $\pm 1°C$. The vertical neck of the reaction vessel was then fitted with a sealed glass stirrer. Its inclined neck(s) was (were) sealed with Suba Seal turnover stopper(s) through which access to the reaction mixture could be gained with a syringe needle without the ingress of atmospheric moisture. The mixture of triol—diglyme was thoroughly stirred for about 30 min.

By means of a graduated hypodermic syringe, an approximately predetermined quantity of acyl chloride was injected into the reaction vessel. The stirrer, which was momentarily stopped to facilitate acyl chloride injection, was restarted, and a stop-clock was started.

Pregelation sampling and determination of gel point

At various times prior to gelation, the extent of reactions was determined as previously described[4]. The onset of gelation was determined by the sudden loss of fluidity in the reaction mixture resulting in the polymer mass (network and sol) produced in consequence of the polycondensation reaction twisting around and rising up the glass stirrer stem (Weissenberg effect).

Post-gelation sampling

Fifteen or more min after the acyl chloride had been injected into the reaction vessel, a portion of the reaction mixture was withdrawn with a hypodermic syringe and distributed into tared conical flasks, sealed with Suba Seal caps, maintained at reaction bath temperature. The number of

such samples taken from a given reaction run depended on the speed of the reaction, that for the more concentrated systems being smaller than for the dilute ones. At various times after gelation was observed in the main reaction mixture, each of these flasks was taken out in turn and the reaction in it was quenched by means of a volume of ethyl methyl ketone/water/acetone mixture (3:1:1) large enough to swamp quickly the network—sol mixture. The extent of reaction at the time of termination of reaction in a sample was determined by analysing the quenched sample first by acidimetry and subsequently by chloride titrimetry.

Extent of reaction at gel point

The extent of reaction at gelation was obtained from conversion—time plots or from second or third order kinetic plots by extrapolation to gel time for systems in which reaction was monitored up to gel point only. For systems monitored beyond the gel point, the extent of reaction at gel time was obtained *via* interpolation of the plots at gel time.

Although post-gelation kinetics of the formation of the polyester networks produced during this study has not been carried out, the method of post-gelation sampling described above provides a means for such studies in the future and has been validated by the results and observations of two experiments described elsewhere[6] which were designed to study by chemical analysis the effect of stirring or otherwise on the progress of polyester network formation. Suffice it here to state that continuous stirring of a gelling system is not essential provided that the reactants have been thoroughly mixed initially.

RESULTS

The three techniques described above for determining gel time concentration of acid chloride gave values of (COCl) which agreed to within 1% (at worst) for the 300K systems. Typical graphs of these techniques are shown in *Figure 1*. As the titrimetric analysis on which these techniques depend had an accuracy of 1–2%, no one of these methods can be said to be better than the other in the light of the results obtained in this study. In general, the second order kinetic plots for these systems were linear, e.g. *Figure 2* while their third order kinetic plots showed an upturn, e.g. *Figure 1*.
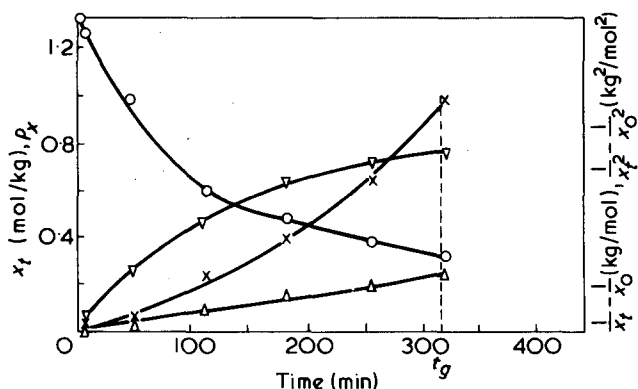

Figure 1 Analytical techniques for determination of acyl chloride concentration at gel point, x_t = acyl chloride concentration at time t; p_x = extent of reaction with respect to acyl chloride. $\bigcirc$, $\triangledown$, conversion—time plots; $\triangle$, second order kinetic plots; X, third order kinetic plots
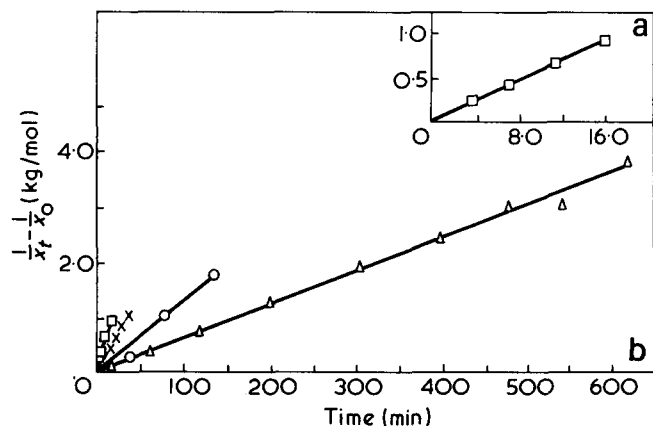
Figure 2 Second order kinetic plots for four reaction runs involving stoichiometric quantities of polymeric triol, LHT240 and sebacoyl chloride in diglyme at 300K. (a) □, 0% diglyme; (b) X, 18% diglyme; ○, 42% diglyme; △, 65% diglyme x_t, x_0 as for *Figure 1*
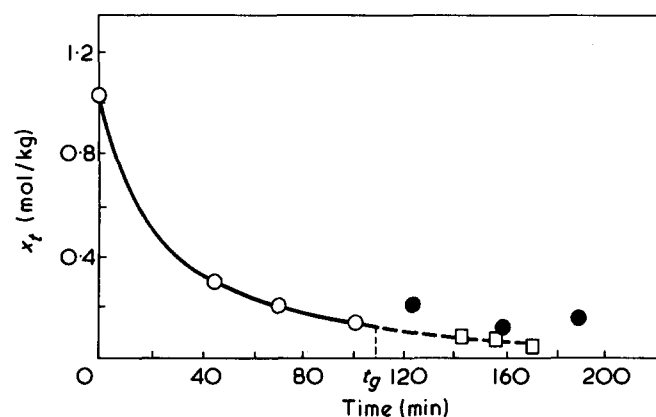

Figure 3 Non-uniformity of reaction mixture arising from post-gelation stirring of reaction system involving polymeric triol LHT 240 and adipoyl chloride in diglyme (69.48% w/w) at 333 K; gel time, 108 min. ○, pregelation samples; ●, post-gelation samples taken from reaction mixture stirred beyond gelation; □, post-gelation samples from whole reaction mixture, x_t, x_0 as for *Figure 1*

These indicate that the reactions studied here are second order and not third order. For the 333K series experiments gelation was not observed for reaction mixture containing 83.57% w/w diglyme; and for 300K series experiments, gelation was not observed for reaction mixture containing 74.46% w/w diglyme. This is ascribed to a high degree of intramolecular reaction, characteristic of highly dilute systems, which inhibits the formation of an infinitely branched network (or gel).

For the 333K systems, the extents of reaction at gel appeared to be excessively high in comparison with the data of Smith and Stepto[4] on a similar system. This is thought to be due to the possibility that the small flanged reaction vessel used for these systems might have permitted the entry of water into the reaction mixture from the reaction bath, or that the reaction mixture was contaminated by some undesirable impurity. Consequently, no reliable quantitative interpretation could be made from these systems. However, qualitative uses were made of their data which showed:

(i) that stirring beyond the gel point made the reaction mixture non-uniform after the gel point, *Figure 3*;

(ii) that the extent of reaction after gelation could be de-

termined by titrimetric analysis using a suitable solvent medium, *Figure 5*;

(iii) that the progress of reaction was independent of stirring provided that the reactants were thoroughly mixed initially, *Figures 4–5*.

DISCUSSION

In view of the literature evidence briefly discussed above, on the kinetics of acyl chloride–alcohol reaction, simple second order and third order kinetic analyses were carried out on the data of the 300K series experiments.

For a stoichiometric reaction which conforms to second order kinetics, the instantaneous concentration, x, of the reaction products is given by:

$$k''t = \frac{1}{b - x}$$

where k'' is the second order rate constant, t is time, and b the initial concentration of one of the reactants. For such a system, the plot of $\{1/(b - x) - (1/b)\}$ vs. t is linear with slope k''. For a stoichiometric reaction mixture which accords with third order kinetics, the relevant expression is

$$k'' = \frac{1}{2}\left[\frac{1}{(b - x)^2} - \frac{1}{b^2}\right]$$

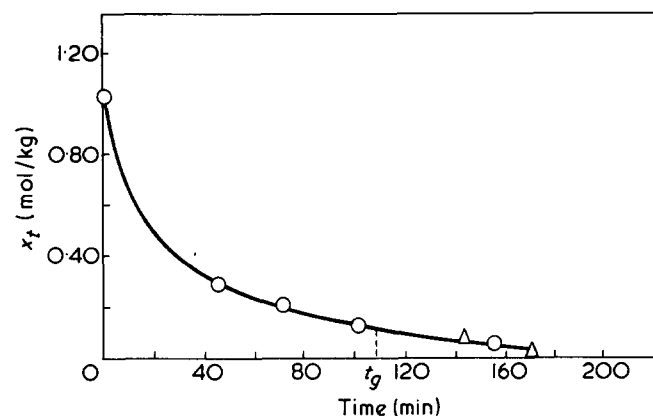where k'' is the third order rate constant and is the slope of

Figure 4 Uniformity of reaction in absence of stirring after initial mixing: ○, stirred reaction system; △, unstirred reaction system. Reaction data as for *Figure 3*
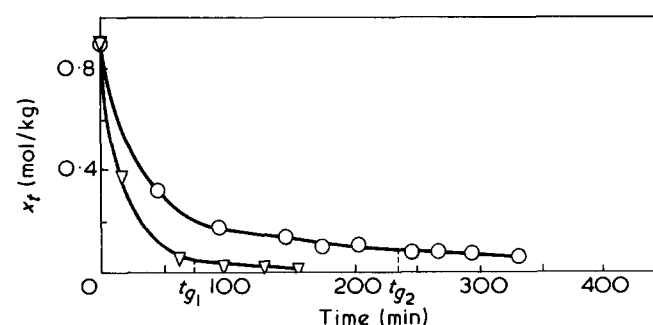

Figure 5 Possibility of titrating sol–network mixtures. ▽, Adipoyl chloride–LHT 240 polymerization in diglyme at 333K, gel time, 74 minutes; ○, sebacoyl chloride–LHT 240 polymerization in diglyme at 333K, gel time = 235 min

a linear plot of $\frac{1}{2}\{[1/(b-x)^2]-(1/b^2)\}$ vs. t.

The data for the reaction between SC and T at 300K presented graphically in *Figure 2* indicate concordance with second order kinetics. Although other workers have reported second and higher kinetic order for polyester formation from polymeric alcohols and acid chloride in ethers and have proposed what appear to be useful explanations for their results[1,2,3] the results obtained in this study which indicate that the reaction between polymeric triols and acyl chloride in diglyme, an ether, at 300K is of second order may be explained by the following simple mechanism due to Roberts and Caserio[7].

According to Roberts and Caserio, the reaction between methanol, (CH$_3$OH), a monomeric alcohol, and acetyl chloride, (CH$_3$COCl), proceeds through the formation of complexes (I) and (II) according to the mechanism:
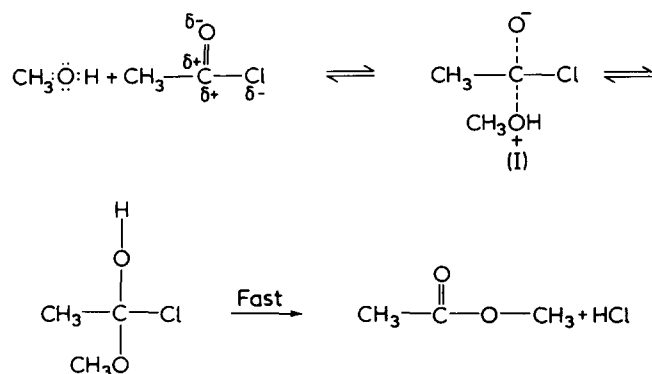

The positive character of the carbonyl carbon of the acid chloride owing to the polarization of the carbon–oxygen and carbon–chloride bonds enables the acyl chloride to be bonded to the alcohol through one of the latter's lone pairs of electrons (on the oxygen of the hydroxyl group) to form complex (I). Complex (I) contains both an acidic group (CH$_3$–O$^+$–H) and a basic group

so that a proton shifts from one oxygen to the other to give complex (II) which rapidly loses hydrogen chloride to form the ester. Roberts and Caserio do not concern themselves with working out the order of reaction but merely suggest that it is an addition–elimination process. Their suggestion accords with the classical definition of condensation processes. That the reaction mechanism accords to second order kinetics is shown as follows by considering the rate equations for all the elementary processes that lead to the reaction products.

If the mechanism is represented schematically by

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_1 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} C_2 \overset{k_5}{\longrightarrow} P \tag{1}$$
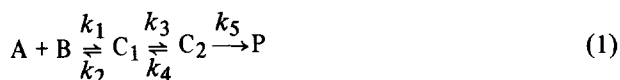
where A is the alcohol, B the acyl chloride, C$_1$, C$_2$ the complexes (I) and (II), respectively and P the products, while k_1, k_2, k_3, k_4 and k_5 are the rate constants associated with the processes indicated, the overall rate of reaction is the rate of appearance of P which may be regarded as the rate of formation of P from C$_2$. This is given by

$$\frac{d[P]}{dt} = k_5[C_2] \tag{2}$$

[C$_2$] depends on [C$_1$] according to the equation:

$$\frac{d[C_2]}{dt} = k_3[C_1] - k_4[C_2] - k_5[C_2] \tag{3}$$

while [C$_1$] depends on [A], [B] and [C$_2$] by the equation:

$$\frac{d[C_1]}{dt} = k_1[A][B] - k_2[C_1] - k_3[C_1] + k_4[C_2] \tag{4}$$

Assuming stationary concentrations for C$_1$ and C$_2$ respectively:

$$\frac{d[C_2]}{dt} = 0$$

and equation (3) yields

$$[C_2] = \frac{k_3[C_1]}{k_4 + k_5} \tag{5}$$

Similarly,

$$\frac{d[C_1]}{dt} = 0$$

and equation (4) yields:

$$k_1[A][B] = (k_2 + k_3)[C_1] - k_4[C_2] \tag{6}$$

Substituting for [C$_1$] from equation (5) in equation (6) leads to:

$$[C_2] = \frac{k_1 k_3 [A][B]}{k_2(k_4 + k_5) + k_3 k_5}$$

which gives the rate of reaction according to equation (2) as:

$$\frac{d[P]}{dt} = \frac{k_1 k_3 k_5}{k_2 k_4 + k_5 + k_3 k_5}[A][B]$$

showing that the reaction is second order, the rate constant k'' being given by:

$$k'' = \frac{k_1 k_3 k_5}{k_2(k_4 + k_5) + k_3 k_5}$$

The extension of the mechanism of formation of simple molecules to polymerization systems has been done previously, and it is generally known that carboxylic acid–alcohol polymerization proceeds in accordance with the same order of reaction as the simple esterification reaction between ethanol and acetic acid under similar conditions[8].

The observation of second, third, and higher kinetic orders previously reported for acyl chloride–alcohol reaction systems may be due to the peculiarities of the respective reaction systems and conditions. Further systematic investigation

of more acyl chloride—alcohol systems at a variety of conditions is suggested.

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