Cross-linking of some Copolymers of Tetrafluoroethylene Through Urethane Bridge by Diisocyanate Reagents; Kinetics of the Addition Reaction

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ABSTRACT

An experimental kinetic study of the addition reaction between hydroxyl groups of some copolymers of poly(tetrafluoroethylene-co-vinyl alcohol) and isocyanate groups as cross-linking agents has been conducted. The kinetics of the cross-linking reaction and the extent of reaction are followed and monitored by infra-red spectroscopy. It is found that the reaction follows a simple second order kinetics until an extent of reaction of 80% and the gel point of 85—90% are reached. For conversion above the gel point, a negative deviation from the second-order kinetics is observed.

Key Words: polytetrafluoroethylene, poly(tetrafluoroethylene-co-vinyl alcohol), cross-linking, kinetics, gelation

INTRODUCTION

The reaction between a monoalcohol and a monoisocyanate leading to the formation of a urethane group is usually well known, though any such combination is a specific case [1]. Over the years, several equations which describe the kinetics of various systems in given experimental conditions have been proposed [2, 3], but as soon as polyfunctional monomers are involved in order to obtain linear or cross-linked polyurethanes in solvent or in bulk, the kinetics of formation become much more complicated. The main reason for complication seems to be a consequence of the rapid increase in viscosity of the reaction medium with the progress of the polycondensation. Another difficulty originates from the reactivities of the isocyanate groups and the hydroxyl functions, which may differ [4, 5].

Model networks have been the subject of many theoretical and experimental investigations [6—14]. In order to study such kinetics, several authors [15—16] have tried to adopt, with more or less success, the kinetic equations established for the monoisocyanate/monoalcohol systems.

Depending on the chemical nature of the polyfunctional reactants and the synthesis parameters, the rate is found to increase or to decrease, usually near the gel point, or not changing at all during the reaction process [17].

The aim of such studies is to understand network formation and to explain some of the properties of the final cross-linked material. It is well known that these properties depend strongly on the pregel region. However, before investigating
the structure and the mechanical properties of the gel, a thorough preliminary chemical study of its formation is necessary, as many parameters play a role in the synthesis of this material. Such knowledge can then allow an optimization of the gelation process.

The present paper deals with a kinetic study of the formation of urethane links, which lead the system to a cross-linked material. To describe the chemical kinetics of the network formation, we used infra-red spectroscopy. The chemical reaction may be followed from its onset to final conversion even when a network is formed. The only prerequisite is the existence of a characteristic absorption peak that follows a well known law in a defined range of concentrations and may be related accurately to the actual monomer content of the reaction medium. In this case, the system follows the Beer-Lambert's law. Thus, we have applied the said method to investigate the kinetics of reaction of some poly(tetrafluoroethylene-co-vinyl alcohol) polymers with toluene 2,4-diisocyanate (TDI), hexamethylene diisocyanate (HMDI), and isophorone diisocyanate (IPDI) as depicted in Scheme 1. These reactions are carried out in presence of triethylamine as the catalyst.

**EXPERIMENTAL**

**Material**

Several copolymers of the same chemical nature were used; the elemental analysis, OH meq of these copolymers and their structures, are given in Table I and Schemes 1, 2. These copolymers were further purified by dissolving in a mixture of 1,2-dichloroethane/methanol solvent and precipitating in distilled water. The precipitated polymer was then dried in a vacuum oven in the presence of phosphorus pentoxide for about 48 h. Three cross-linking agents were used: toluene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI), and hexa-
Table 1. Elemental analysis and hydroxy milli-equivalent of copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>F (%)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>OH* (meq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB-6</td>
<td>TFE/Et/Vina</td>
<td>46.3</td>
<td>37.9</td>
<td>3.9</td>
</tr>
<tr>
<td>AB-7</td>
<td>TFE/Et/Vina</td>
<td>30.9</td>
<td>44.2</td>
<td>4.3</td>
</tr>
<tr>
<td>AB-2</td>
<td>TFE/Va</td>
<td>-</td>
<td>40.5</td>
<td>4.9</td>
</tr>
<tr>
<td>AB-5</td>
<td>TFE/Et/Vina</td>
<td>34.5</td>
<td>41.8</td>
<td>4.3</td>
</tr>
<tr>
<td>AB-10</td>
<td>TFE/Vina</td>
<td>-</td>
<td>42.9</td>
<td>4.1</td>
</tr>
<tr>
<td>AB-13</td>
<td>TFE/Vina</td>
<td>-</td>
<td>45.9</td>
<td>4.6</td>
</tr>
</tbody>
</table>

* Concentration of OH, in milli-equivalent, in 1.0 g of polymer.

TFE: tetrafluoroethylene; Et: ethylene; Vlne: vinyl acetate; VA: vinyl alcohol.

methylenediisocyanate (HMDI) which were provided by Merck and were used without further purification. The catalyst, triethylamine, was used as received. Cross-linking reactions were carried out in dry N,N-dimethylformamide (DMF).

Stoichiometry

The functionalities of the copolymers were determined with good accuracy by acetic anhydride-pyridine method [18].

The stoichiometric ratio was calculated directly from the number of reactive groups present in the copolymers.

Sample Preparation

The samples were prepared at constant temperature under dry nitrogen gas by first dissolving the polymers in anhydrous DMF at a 25% concentration by weight, and then, the catalyst was added at a 1.5–3.0% concentrations by weight with respect to the polymer precursors. The cross-linking agents were added to the mixtures in stoichiometric amounts. After mixing the reagents, the solution was injected into an infra-red cell. The final products were colourless and transparent.

Measurements

The reaction mixture was injected into an infra-red solution cell. The path length was checked by a tetrafluoroethylene spacer (50 μm) within the range in order to prevent the strong isocyanate absorption band from going out of scale. This thin part also ensured isothermal conditions throughout the reaction.

Scheme II. Reaction of hydroxyl functions and isocyanate groups; network formation.
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The kinetics of the addition reaction was followed by infra-red spectroscopy, and one spectrum could be recorded every 30 seconds during the gelation process. The characteristic isocyanate absorption band at the wavenumber of 2273 cm$^{-1}$ (Figure 1) shows a gradual decrease due to the consumption of the isocyanate during the gelation process.

The absorption data can be related to the extent of reaction according to Beer-Lambert's law. The reaction conversion was calculated from the change of the normalized absorbance of the isocyanate peak as a function of time. For each experimental point, the following equation defines the extent of reaction $p$ at a time $t$ of the reaction.

$$p = (A_\infty - A)/A_\infty$$

where $A_\infty$ is the NCO peak area of the unreacted medium and $A$ the peak area corresponding to subsequent reaction times. The broad peak remains constant during the course of reaction, and its value was used as an internal standard. In the same spectrum we observe the evolution of the C=O band at 1731 cm$^{-1}$ (stretching vibration) and of the N–H band at 1544 cm$^{-1}$ (deformation vibration), which are characteristic of a urethane linkage (Figure 2).

The recorded kinetics of some reacting copolymers are shown in Figures 3–5, where the conversion $p$ was plotted as a function of time $t$. It was observed that the reaction is very fast at the beginning of the reaction, and at longer times the addition reaction slows down, and finally the extent of reaction tends towards a limit. From this point on we can suppose that chain coupling is more and more difficult. In this study the kinetics of the addition reaction is followed up to a conversion of...
RESULTS AND DISCUSSION

Kinetics in the Pregel Region

In order to predict a simple reaction order, according to J.B. Herz and coworkers report [19], let us consider a two species system that are shown as A and B. These particles diffuse and upon colliding form an inert species C. In this system mobility is an important factor. The latter depends on the viscosity of the medium. In our system the reaction between the hydroxyl-containing polymers and diisocyanate leads to increasing viscosity. Thus the diffusion mechanism, which becomes a predominant factor and determines the kinetics of the reaction and the diffusion limited process, is considered for these systems.

This two-species collision process is symbolically presented by:

\[ A + B \rightarrow C \]

with \( k \) as rate constant. In the mean-field limit [20–23], the kinetics are described by the simple rate equations for the concentrations \( CA(t) \) of A particles and \( CB(t) \) of B particles at time \( t \):

\[ \frac{dCA(t)}{dt} = \frac{dCB(t)}{dt} = -kCA(t)CB(t) \]

If the initial concentrations of A and B, at the beginning of the reaction, were equal i.e.,

\[ CA(0) = CB(0) \]

the solution of the above differential equation is an algebraic decay:
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Figure 3. Extent of reaction p versus time t of isoc-15 (0.25 g AB-6, 6.25 µl TEA, 217 µl TDI, T=31–32 °C).

CA(t) = (kt + CA(0))^(-1)

which is the mean-field prediction for the decay of concentration of the species A versus time.

Since the only reaction that is carried out at constant temperature is the reaction of hydroxyl groups and isocyanate, the variation of the NCO concentration can be related directly to this reaction:

R-OH + R'-NCO → R-O-CO-NH-R'

The urethane function that is formed is stable, and this reaction exhibits second-order behaviour according to mean-field limit. The plot of 1/(1-p) versus time t for some of reactions are shown in Figures 6–8. It is observed that the reaction cannot be described by simple second-order kinetics.

In the presence of a catalyst like triethylamine, the reaction scheme could be shown as below:

R-OH + R₃N → R-OH .... NR₃

| 
| 
| R'-NCO

R-O .... H .... NR₃

OC .... N-R'

R₃N + OC-N-R'

Thus, as suggested in the mechanism above, the amine catalyst is not in direct contact with the isocyanate group. In this scheme, and provided the respective concentration of NCO and OH groups are in stoichiometric ratio, the rate equation in the mean-field limit can be written as follows [24]:

\[-\frac{d[NCO]}{dt} = k[NCO][R₃N] = k'[NCO]^2\]  (1)

The catalyst concentration was included in rate constant. The solution of eqn (1) is:

\[[NCO] = (k't + \frac{1}{[NCO]_o})^{-1}\]  (2)

In terms of the extent of reaction p defined as \([NCO]=[NCO]_o(1-p)\), eqn (2) can be written:

\[1/(1-p) = k'[NCO]_o t + 1\]  (3)

Figure 4. Extent of reaction p versus time t of isoc-7 (0.25 g AB-6, 12.5 µl TEA, 250 µl HMDI, T=31–32 °C).

Figure 5. Extent of reaction p versus time t of isoc-37 (0.25 g AB-6, 6.25 µl TEA, 317.6 µl IPDI, T=31–32 °C).
In this research we have observed second-order kinetics up to a conversion of 80%.

The slope of the linear part of Figure 6 represents a characteristic time $\tau$ for the gelation process.

$$\tau = \frac{1}{k[R_3N][NCO]}$$

where, $k$ is rate constant and $[R_3N]$ is the catalyst concentration.

**Kinetics in the Postgel Region**

The reaction was followed by second-order kinetics up to about 80% conversion, which represents approximately the gel point. Above the gel point the reaction follows a different kinetic behaviour.

The kinetic curves deviate negatively from the straight line. The principal difficulty encountered comes from the strong viscosity increase in the reaction medium [25]. Changes in the apparent reaction rate for the reaction of isocyanates with alcohols were frequently observed by several authors [26-30].

**CONCLUSION**

The results obtained in our investigation are in an excellent agreement with those reported earlier [19, 29, 30]. Though a reaction that involves a gelling process is rather complex, the kinetics of the cross-linking reaction can be followed by infra-red spectroscopy, provided that one of the reacting groups has a characteristic absorption band. The extent of reaction can be easily monitored by this technique. By this method, we have established that the reaction between hydroxyl groups of co-polymers and the isocyanate groups of cross-linking reagents follows second-order kinetics until about 80% conversion (pregel region). For conversion above the gel point we observe a negative deviation from the second-order kinetics; it means that the reaction rate decreases, and this could be due to increase in viscosity of the medium.

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