An experimental study of polyurea membrane formation by interfacial polycondensation

S.J. Wagh, S.S. Dhumal, A.K. Suresh

Department of Chemical Engineering, Indian Institute of Technology, Powai, Bombay 400076, India

Abstract

Interfacial polycondensation has been studied for many applications, and most importantly for such niche applications such as microencapsulation and membrane synthesis. The fast kinetics and the complexity of the process involving the interplay of several rate and equilibrium processes make it difficult to study the reaction and explore the effect of kinetics on the properties of the polymer film that forms. We show in this study that a dispersed phase configuration such as used in microencapsulation, with a fast on-line pH measurement, is a convenient way to study these reactions. Apart from the ease of obtaining kinetic information, the technique results in self-supporting films which can be recovered and characterized for structure by a variety of techniques. In this study, the intrinsic variables which influence observed reaction velocities, such as reactant concentrations and film thickness, have been varied through experimental parameters that can be more conveniently set. Although the intrinsic kinetics is fast, it is still possible that intrinsic chemical kinetics play a significant role in the overall mechanism, since the films formed are very thin. Data obtained under such conditions, with an excess of the organic-side monomer (hexamethylene-1,6-diisocyanate, HMDI), show a first order dependence of monomer consumption rate on the aqueous-side monomer (hexamethylene-1,6-diamine, HMDA). The effect of solvent on the observed rates shows some interesting characteristics, counterintuitive if a correlation is sought with the partition coefficient of HMDA into the solvent. It is shown that rates correlate better with solvent polarity. The polymer formed is of low molecular weight in general. The molecular weight shows a dependence on the mole ratio of monomers, with a ratio (HMDI/HMDA) slightly in excess of 1 being the most conducive to molecular weight development. The polymer is of semicrystalline structure, with the crystallinity determined by the conditions of reaction. These findings are of interest to applications such as controlled release and membrane separations, in which permeation rate through the membrane is of importance.

1. Introduction

Interfacial polycondensation (IP) is a technique of step polymerization by which a polymer product is obtained under ambient conditions of temperature and pressure, and with less stringent needs of monomer purity than in conventional (homogeneous) step polymerization processes. The technique delivers a product in different forms such as encapsulated active principles, thin films, and membranes for several applications, with minimal post-processing. The relative ease of IP has made it an important technique in such applications as the synthesis of thin film composite membranes [1,2] and encapsulation of inks, insecticides and drugs [3]. However, quantitative understanding of IP lags behind that of other established techniques, such as melt and solution polymerization. Experimental information on the influence of preparation conditions on polymer film properties, such as the molecular weight, crystallinity, permeability, etc., is scanty [4,5]. Other work, for example on membrane casting from polymer solutions, shows that the film microstructure, and consequent properties such as film density and permeability are affected significantly by the polymer precipitation mechanism [6]. Thus, clear insights into the kinetics of IP and polymer precipitation mechanism are essential in order for rational design of processes for IP products to evolve.

Early systematic studies on IP were carried out by Morgan and co-workers at DuPont, and Morgan [7] has summarized this work. The important parameters which affect the IP reaction have been identified and the properties of the product have been described here, and these include monomer concentration ratio, nature of the organic solvent and the surfactant used. The reaction, since it employs highly reactive monomers, is extremely fast and this poses problems in measurement of rates. Yadav et al. in their studies on microencapsulation in polyurea shells devised a simple on-line pH
Their work demonstrated the potential of the technique in following fast kinetics in a system of this kind, but the potential could not be fully realized because of the discrete nature of the measurement. While it was generally believed that the reaction rate is controlled by diffusion through the formed polymer, these authors showed that, at least in the case of microencapsulation, it is possible for the reaction to be controlled by kinetics, and still form a coherent film. In their theoretical analysis, these authors used a lumped kinetic approach for the multi-step polymerization reaction, which assumed the reaction to be first order in each of the monomers. In later work, the complete kinetics with no lumping was treated, but with the equal reactivity hypothesis. These authors further considered in some detail, the kinetics of the film formation, the mechanism of polymer precipitation and the molecular weight distribution of the polymer.

The above studies consider the process of IP to be essentially one of diffusion (of one of the monomers) through the film being in series with chemical reaction and phase separation events. Some recent theoretical and simulation studies [11,12] propose an alternative mechanistic picture in which the reaction intermediates (the oligomers) diffuse away from the site of reaction, reacting with other oligomers and the monomers as they diffuse. There is no explicit phase separation leading to film formation in such mechanisms, and what can be called the ‘film’ is the region occupied by the oligomeric species. At present however, the experimental data available is not sufficient to conclusively support or negate either picture. Berezkin and Khokhlov [13] point out the urgent need for a detailed/systematic experimental and theoretical study of IP reaction mechanism for the effective development of IP modeling approach. The present experimental study is in part motivated by this lacuna that exists in the literature, and is meant to clarify the various mechanistic aspects of the IP reaction such as solvent effect, dependence of overall kinetics on the experimental variables, etc.

Not surprisingly, factors controlling functional properties, such as the permeability of the membrane formed, have elicited considerable research interest. In studies on water-loaded microcapsules of different homopolymers, the permeability of the microcapsule membranes towards the solute has been found to be dependent on capsule size, chemical structure of polymers constituting the membranes and solutes, and composition (in the case of homopolymer mixtures) [14]. With polyurea microcapsules, a variation in permeability by an order of magnitude could be achieved by varying the crystallinity of the polyurea [15]. The reaction kinetics seems to be important in controlling the crystallinity—there being a rough inverse correlation between rate and crystallinity [5,9,16]. The role of surfactants and interfacial tension in controlling particle structure has been sought to be explained based on thermodynamics [17].

The locale of the reaction has been debated in the literature. MacRitchie [18] suggested that the reaction takes place in a mixed interfacial monolayer between adsorbed monomer molecules. But most of the researchers report that the polymer forms and grows on the organic solvent side of the interface with no evidence of polymerization in the aqueous phase [7,19]. While the importance of the organic medium (used as a solvent for one of the monomers) was noted in the literature [7,20,21], not much quantitative information has appeared in the literature since, especially in relation to kinetics. Since on balance, the evidence suggests the reaction to take place on the organic side of the interface, the solvent properties would be expected to be important in determining not only the film structure but also the kinetics. The literature on homogeneous reactions shows that in general, solvents influence reaction rates, because of interactions between reactant and solvent molecules [7,20,22–27]. For example, the reaction rate between benzoyl chloride and aniline becomes slower with decreasing polarity (dielectric constant) of the solvent. Although similar reactions and solvents are involved in interfacial polyamidation [7,20,21], we may expect the effect of the solvent to be more complex because of the heterogeneous nature of the system—for example, as Kondo [19] points out, a solvent in which the aqueous phase monomer is able to partition better would give higher rates than one in which the partitioning is poorer. Further, the intrinsic kinetics of polymerization could influence the rate of phase separation and the structure of the film that forms, and there could therefore arise an indirect influence on the observed rate. Thus it seems to be important to clarify the nature of influence of the organic solvent used, on various aspects of the IP reaction.

In the present paper we report an experimental study on the influence of the preparative conditions on the kinetics and product properties, in the IP reaction of hexamethylene-1,6-diamine (HMDA, the aqueous phase monomer), and hexamethylene-1,6-diisocyanate (HMDI, the organic phase monomer). The reaction is

\[
\text{HMDI} \quad \text{HMDA} \quad \text{Polyurea}
\]

The reaction differs from most other step polymerization reactions in that no small molecule such as H2O or HCl is eliminated. Detailed kinetic information has been obtained over a range of operating variables using an on-line pH probe with a data-acquisition system, which makes it possible to follow the fast process with ease. The effect of the organic solvent has been studied by employing several solvents for the organic phase monomer. These solvents have, between them, more than a fivefold difference in their partition coefficient values for HMDA based on literature reports. The partition coefficients under the conditions of relevance have been experimentally determined and show a similar spread in values. The product, polyurea, has been characterized by a variety of techniques such as viscometry (for molecular weight), DSC and XRD.

2. Experimental studies

HMDA of purity >99% and HMDI of purity >98% were both obtained from Fluka, Switzerland, and used without further purification. Solvents for HMDI and other chemicals used in the preparation of samples were of analytical reagent grade and were obtained from firms of repute. Distilled water was used as the solvent for HMDA. The emulsifier Tween-85 (Fluka, Switzerland) was used to stabilize the o/w emulsions in which the reaction was carried out. In some experiments, sodium lignosulfonate (instead of Tween-85) was used as the surfactant since it was found that microcapsules thus formed were better able to maintain their shape under the sample preparation procedures used for electron microscopy. The experimental procedure followed for the preparation of polyurea microcapsules was in general similar to that reported earlier [8,9]. A two-step procedure was adopted to ensure that the drop size distribution was the same in all the experiments. In the first step, a concentrated oil-in-water emulsion (oil:water = 1:2, v/v) was prepared by dispersing the organic phase—a solution of the desired concentration of HMDI in the solvent of interest—in distilled water, with Tween-85 (4%, v/v, of the distilled water) as the emulsifying agent. The emulsification was carried out by stirring the phases together in a beaker at 3000 ± 20 rpm for 15 min, with a shrouded, four-bladed, pitched turbine impeller. This step was identically performed for all the experiments except for the concentration of HMDI in the organic phase, which was chosen according to the needs of the experiment. This was found to result in the same drop size distribution in all experiments [9] as...
shows a typical calibration plot. In earlier work [8, 9], we had com-
tionship is satisfactorily expressed by an equation of the form:

\[ \text{slope} = \frac{1}{p} = 0.6708 \]

Fig. 1. A typical calibration plot showing the relationship of solution pH to HMDA concentration, and the linear fit of the data.

determined by particle size analysis on the emulsion as well as on the microcapsules after the encapsulation experiment. In the sec-
ond step, an appropriate volume of this emulsion, depending on the required phase volume ratio, was added to an aqueous solution of HMDA held in a beaker, under conditions of mild stirring. The beaker was also equipped with a thermometer, and a pH probe, connected through a pH-meter, to a data acquisition system. The time of completion of addition was taken as the start of the reaction. Since HMDA solution is alkaline, its consumption is accompanied by the pH becoming nearly constant. At this point, the agitation was stopped and the microcapsules were filtered out.

Calibrations of pH as a function of the concentration of HMDA in the pH range of interest (9–12.5) were prepared from time to time using standard solutions of known HMDA concentrations. Fig. 1 shows a typical calibration plot. In earlier work [8,9], we had compared such experimental calibrations with the theoretically derived relation between pH and concentrations for pure HMDA solutions, and shown that over the range of experimental interest, the relationship is satisfactorily expressed by an equation of the form:

\[ C_A = A h^{-p} \]  

where \( C_A \) is the concentration of HMDA, \( h \) is the hydrogen ion concentration, \( A \) and \( p \) are calibration constants. While the value of \( A \) tended to vary somewhat, \( p \) was relatively constant in the range 1.3–1.55. It has been shown in earlier work [9] and will be seen that it is only the value of \( p \) that is needed for interpretation of kinetic data.

A fast response of the pH probe is of the essence in getting reliable kinetics, since the reaction is quite fast. The probe response was measured by administering a step change in pH (by shifting the probe quickly from one pH to another) and recording the response with the data acquisition system. Considerable attention was given to maintaining the probe surface clean between experiments. As with the calibration, the speed of response of the pH probe was checked periodically.

All reactions were carried out at temperatures of 28–30 °C. The emulsion formed in the first step of the experimental procedure was of sufficient stability that the drop size distribution remained constant over the timescale of encapsulation. The final capsule size distribution was therefore determined by this initial distribution which, as described before, was kept the same in all the experiments. The size distribution of capsules was determined in randomly selected experiments, in a particle size analyzer, Galai CIS-1 (range of measurement 0.5–150 μm) and Brookhaven Zeta Plus (range of measurement 2 nm to 3 μm).

In a system of this kind, the intrinsic variables (‘process variables’) that might be expected to influence the kinetics (and hence the properties of the polymer film) are the concentrations of the monomers, the interfacial area per unit volume, and the thickness of the film that forms. In our work, a wide range of these variables has been covered by employing a set of ‘experimental variables’ that are more convenient from a practical viewpoint. These are: the phase volume ratio \((V_d/V_c)\), number of moles of limiting monomer per unit volume of dispersed phase \((n_l/V_d)\), and the monomer mole ratio \((R)\). Table 1 shows how the experimental variables are related to the process variables. Experiments were conducted for three different values of the phase volume ratio \((V_d/V_c)\): 0.045, 0.1 and 0.25. At each volume ratio, a range of recipes was used that allowed the mole ratio of the monomers to be varied from 0.2 to 5, and \(n_l/V_d\) over at least an order of magnitude. The mole ratio of monomers is an important parameter in its own right that controls the molecular weight achievable, and \(n_l/V_d\) controls the film thickness (nominal, as calculated from stoichiometry and swelling considerations). A fivefold variation in the interfacial area per unit volume and a tenfold variation in the final film thickness could thus be achieved in the experiments. The concentrations of HMDA used were such that a reasonable variation in pH would be expected whenever HMDA was the stoichiometrically limiting monomer \((R > 1)\).

To examine the effect of the solvent for the organic phase monomer on various aspects of the reaction and the product formed, two solvents, cyclohexane and carbon tetrachloride, were used for HMDI. Literature notes the importance of the partitioning of the amine into the organic phase in determining the kinetics [7,19]. The partition coefficients in these solvents, reported in NaOH solutions, differ by a factor of about 5 [7]. Some experiments were also conducted in toluene and p-xylene to clarify certain aspects of kinetics. Since our experiments employ aqueous solutions without added alkali, the partition coefficients in all solvents of interest were experimentally determined by the shake-flask method. The aqueous and organic phases, separated from shake flask after equilibration, were titrated against a known concentration of HCl with methyl orange as an indicator to determine concentrations.

Samples of polyurea for various characterization studies were prepared as in previous work [5]. The microcapsules were first washed with distilled water and then with methanol several times (4–5 washes each) to eliminate traces of unreacted monomers. These microcapsules were then dried in an oven at 70 °C. Some of the dried sample was preserved for SEM analysis and the remaining was ground with a mortar and pestle and taken for various characterization studies described below.

Attempts to determine molecular weight distributions were not very successful because of the insolubility of polyurea in most solvents, and hence, intrinsic viscosity (of solutions of polyurea in 98% sulfuric acid) has been taken as a measure of polymer molec-
Table 2
Experimental conditions for viscosity determination.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>25 °C</td>
</tr>
<tr>
<td>Solvent</td>
<td>98% H$_2$SO$_4$</td>
</tr>
<tr>
<td>Viscometer</td>
<td>Ostwald–Fenske</td>
</tr>
<tr>
<td>Sample volume</td>
<td>20 ml</td>
</tr>
<tr>
<td>Concentration</td>
<td>0.5 g/dl</td>
</tr>
<tr>
<td>Efflux time for pure solvent</td>
<td>153.53 s</td>
</tr>
</tbody>
</table>

Molecular weight. Viscosities of polyurea solutions were determined under the conditions shown in Table 2. The intrinsic viscosity values were evaluated by the one point determination method [28]. Determination of viscosity of the polymer solutions was done by the conventional procedure of measurement of efflux time of the solution in an Ostwald–Fenske viscometer.

Differential scanning calorimetry (DSC) of the polyurea samples was carried out on a DuPont 2100 machine in the range of temperatures 20–300 °C at a heating rate of 10 °C/min. The powder X-ray diffraction (XRD) patterns of the polymer samples were recorded in the reflection mode on a wide angle X-ray (WAXS) diffractometer using a Rigaku goniometer. Scanning electron microscopy (SEM, in a Hitachi S3400) was used to visualize the shape of the microcapsules formed.

The reproducibility of the experimental procedure was checked by repeating some runs in their entirety. In such runs, the reproducibility of the characterization procedures was also established by carrying out the analysis steps (i.e. viscosity, DSC and the XRD analyses) separately for each of the duplicates.

3. Results and discussion

Fig. 2 shows the SEM micrographs of the sodium lignosulfonic acid (SLS) based and Tween-85 based microcapsules prepared with $R = 1$, $V_d/V_c = 0.045$ and $n_L/V_d = 0.606$ kmol/m$^3$. The SLS based microcapsules are spherical in shape with a size distribution ranging from 2 to 25 μm. A multivalent salt, CaCl$_2$, was used in these experiments to stabilize the microcapsule structure by interacting and physically cross linking the SLS chains [29]. Some reaction between the amine monomer and the surfactant is also possible, and could contribute to the rigidity of the capsule wall. Capsules formed with Tween-85, where such rigidification of the capsule wall is not done, were more likely to deform under the sample preparation protocols (especially drying) used for SEM study, as seen in the figure. Most of the other studies (especially kinetics) however, were carried out with Tween-85 microcapsules.

3.1. Influence of experimental variables on process kinetics

The effect of the selected experimental variables on the kinetics was qualitatively similar in the case of the two solvents (cyclohexane and carbon tetrachloride) with which most of the experiments were carried out. In what follows therefore, we illustrate the effect of the parameters studied using the experiments with cyclohexane.

Fig. 2. SEM pictures of the microcapsules formed using (a) SLS as surfactant and (b) Tween-85 as surfactant.
first, and then describe the effect of solvent. Experiment numbers prefixed with S and T refer respectively to experiments with cyclohexane and carbon tetrachloride as the solvent.

Fig. 3 shows a typical progress of reaction in terms of the (measured) variation of pH and the (calculated) variation of diamine conversion with time. The data are for an encapsulation experiment with cyclohexane as the organic medium and with a mole ratio (isocyanate to amine) of 5. As in this case, reactions with high initial concentrations of the monomers (large values of \( n_R/V_0 \) and \( R \)) proceeded very fast. After a brief period (of the order of a second) of initial adjustment, the pH falls rapidly (in this case, more or less linearly) with time. Eq. (1) shows that the conversion of the amine is related to the fall in pH from the initial value:

\[
X = 1 - \left( \frac{h}{h_0} \right) = 1 - 10^{-(\text{pH}_0 - \text{pH})p}
\]  

For \( p = 1.3 \), this equation gives conversions of about 95%, 99.75% and 99.99% for a fall of 1, 2 and 3 units in pH, respectively. The conversion of amine attained during the linear period is thus well above 99%, so most of the reaction is completed in this phase. HMDA being the stoichiometrically limiting monomer by far, the pH is seen to ultimately reach neutral values, indicating total exhaustion of amine. In experiments with \( R \) values of 1 or less, the pH leveled off at values above 7. The pH curve shows a second acceleration towards the end of the reaction (beyond 99.9% conversion of the amine). The appearance of this kind of a ‘hump’ was a very reproducible feature always occurring in the pH range of 9.3–7.3. This was initially thought to be indicative of some mechanism-related event, but repeated experiments have not shown any evidence of this and it is now thought to be a result of the nature of nonlinearity of the pH–concentration relationship in this pH range.

Eq. (2) suggests that the rates of the reaction under different conditions can be compared on the basis of the rate of fall of pH from the initial value. Fig. 4 compares the rates of reaction for two experiments on this basis, the experimental conditions being identical except for the value of \( R \), which is 1 for one experiment (S7) and 5 for the other (S18). For \( R = 1 \), we would expect both monomers to be consumed completely, but the result in Fig. 4 indicates that the amine is not completely consumed, the conversion at the end of the reaction being about 90%. Since three types of oligomers are in general expected to form in such polymerizations depending on the end groups (oligomers in which both ends are amine, those in which both ends are isocyanate, and those in which one end is amine and the other isocyanate), the observed behavior indicates a dominance of the isocyanate ended species. This would lead to an excess of isocyanate groups being reacted as compared to amine groups, and consequently an exhaustion of the diisocyanate monomer before the diamine. This event is likely if the reaction takes place on the organic side of the interface, and is more difficult to explain if the reaction takes place in an interfacial region with ample opportunity for the isocyanate ends to be capped by the diffusing amine monomer. That the polymer formed is of low molecular weight is also indicated by these results, since an imbalance in the end groups will have a noticeable effect on the overall stoichiometry only under these conditions. The final pH attained in experiments with \( R \leq 1 \) thus gives an indication of the molecular weight and effective stoichiometry of monomer consumption.

A differentiation of the calibration function (Eq. (1)), gives the following relation between the rate of fall of monomer A concentration and the rate of fall of pH:

\[
\left( \frac{1}{C_A} \right) \frac{dC_A}{dt} = 2.3026 \frac{dpH}{dt}
\]  

The initial part of the pH curves for the experiments shown in Fig. 4 are replotted in Fig. 5, and show the linearity (remarked upon above), quite clearly. The data shown for run S7 go up to a conversion of 75%, and, in the case of S18, up to 99%. In view of equation (3), the data therefore suggest an overall proportionality of the rate on the concentration of A over a large conversion range. The two experiments were conducted with identical initial concentrations of the diamine, but with different diisocyanate concentrations. The considerable influence of the diisocyanate concentration on the rate is indicative of the reaction being on the organic side. Further, any diffusion limitations (for transfer of the diamine to the site of reaction) are also seen to be negligible under these conditions. While the role of the monomer concentrations can thus be understood in a qualitative sense, a more detailed understanding would require a modeling of the situation considering the multi-step polymerization reaction, phase separation and its influence on the reactive group concentrations, etc.

Fig. 6 shows the effect of phase volume ratio on the kinetic behavior. As Table 1 shows, the phase volume ratio influences the interfacial area as well as the initial concentration of HMDA, both
Fig. 5. pH–time data for the linear part for the experiments shown in Fig. 4. The best-fit straight lines have slopes of 0.024 (S7) and 0.40 (S18).

of which are higher for the case of S25. The runs shown in the figure are for $R = 0.8$, i.e. HMDI is the limiting monomer. The variation in the concentration of B during the experiment has an influence on the kinetics in this case, as seen by the restricted linear range of the profiles. The final conversion achieved in both cases was the same. The ‘interfacial’ character of the reaction is clear from the substantial influence of the interfacial area in this figure.

Fig. 7 shows the effect of $n_L/V_d$ on process kinetics. The moles of limiting monomer limit the amount of polymer that is formed, and this ratio therefore determines the final film thickness (see Table 1). The experiments being compared were conducted under identical values of the other parameters, but because of the difference (by a factor of 5) in the number of moles of limiting monomer (HMDA in this case), differ in the final thickness of the film. The kinetics are very similar till very late stages of the reaction, the experiment with the smaller $n_L/V_d$ exhibiting a higher rate towards the end. It is possible that diffusion limitations are responsible for lowering the rate in the case of the thicker film. The results indicate that such limitations become important only towards the very end under these conditions. In other similar sets of experiments where the differences in $n_L/V_d$ were smaller (say 30–40%), the kinetics were virtually reproduced over the entire range of pH. Further, when CCl₄ was the solvent, even large differences in film thickness did not lead to differences in rate. It thus appears that diffusion limitations were less likely with CCl₄. The reasons may have to do with differences in film structure and/or differences in intrinsic reaction rates. It will be shown below that the reaction is intrinsically slower in CCl₄ as compared to cyclohexane.

3.2. Effect of solvent on kinetics

Fig. 8 (a)–(c) shows the effect of solvent (for HMDI) on the observed kinetics at three different combinations of the experimental variables. The rate is seen to be higher for cyclohexane than for CCl₄ in all cases. Based on the reported values of the partition coefficient for HMDA from aqueous solutions into these solvents, the availability of HMDA is expected to be about five times higher in the case of CCl₄ compared to cyclohexane, so these results are difficult to explain on the basis of partition coefficients. The reported partition coefficients are however in the presence of NaOH [7]. Partition coefficients between pure HMDA solutions and the solvents of interest were therefore experimentally determined and the values are shown in Table 3. The results show that the partition coefficients are very different when NaOH is present is the aqueous phase;

![Fig. 6. Influence of phase volume ratio on kinetics, other conditions being identical ($R = 0.8$ and $n_L/V_d = 0.5$ kmoles/m³).](image)

![Fig. 7. Influence of the parameter $n_L/V_d$, which determines the final film thickness, on kinetics (other conditions $R = 5$ and $V_d/V_c = 0.045$).](image)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Partition coefficient $b$</th>
<th>Dielectric constant ($\varepsilon$) $[16]$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>Literature</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>320</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td>158$^a$</td>
<td></td>
</tr>
<tr>
<td>p-Xylene</td>
<td>81</td>
<td>50</td>
</tr>
<tr>
<td>CCl₄</td>
<td>53</td>
<td>35</td>
</tr>
<tr>
<td>Toluene</td>
<td>56</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ In presence of NaOH (0.44 M HMDA with 0.9 M NaOH).

$^b$ Partition coefficient = (aqueous phase concentration/organic phase concentration) at equilibrium.
Fig. 8. Effect of solvent on the IP reaction kinetics under different experimental conditions. The reaction is faster in cyclohexane under all conditions. Experimental conditions: (a) $R = 5.0$, $V_d/V_c = 0.1$, $n_L/V_d = 0.4$ and $C_{A0}/C_{B0} = 0.02$; (b) $R = 4.0$, $V_d/V_c = 0.1$, $n_L/V_d = 0.5$ and $C_{A0}/C_{B0} = 0.025$; (c) $R = 2.0$, $V_d/V_c = 0.1$, $n_L/V_d = 1.0$ and $C_{A0}/C_{B0} = 0.05$.

Fig. 9(a) and (b) shows the kinetics observed in experiments with these solvents. Clearly, there is some other effect at play here apart from HMDA availability in the reaction zone.

In order to confirm these trends, experiments were conducted using some other solvents as well, such as p-xylene and toluene. Partition coefficients for HMDA, determined in these solvents, are also shown in Table 3. The partition coefficients are seen to be in the order: cyclohexane > p-xylene > toluene > carbon tetrachloride. Fig. 9(a) and (b) shows the kinetics observed in experiments with these solvents. Clearly, there is some other effect at play here apart from HMDA availability in the reaction zone.

In general, it is possible for the solvent to influence the kinetics of a reaction in various ways, depending on the interactions between solvent and reactant molecules. According to the Hughes–Ingold rules for solvent effect on reaction kinetics [27], if the charge density is lower in the activated complex than in the initial reactant molecule(s) for a reaction, the rate of such a reaction decreases with an increase in solvent polarity. Hsu and Lee [26] concluded that the polarity of the solvent might have a strong effect on the polyurea reaction kinetics (under homogeneous conditions). Table 3 also gives the dielectric constant, a measure of solvent polarity, for the solvents of interest. It is seen that the experimentally observed trends in pH kinetics correlate well with values of the dielectric constant, with the rates decreasing with an increase in solvent dielectric constant. It is thus possible that Hughes–Ingold rules are operative here. Similar trends, i.e. decreases in the rate constants with an increase in solvent polarity, have been observed in other work [22–25] on homogeneous reactions of a similar type. These authors interpreted the solvent effect on kinetics in terms of the solute–solvent interactions due to polarity and hydrogen bonding.
Fig. 9. Solvent effect on reaction kinetics: variation of (a) \((pH_0 - pH)\) and (b) HMDA concentration with time for four different solvents \((n/L/V_d = 0.0202, \, R = 1.0\) and \(V_d/V_c = 0.045)\).

Incidentally, similar values for the ratio of the rates in cyclohexane and carbon tetrachloride were observed [23,24], as the values found in this work.

Our results thus show that it might be erroneous to predict relative rates of IP reactions on the basis of partitioning of the aqueous phase monomer alone, as often done in the literature. Since a choice of solvents is available for applications such as the manufacture of thin film composite membranes, a knowledge of relative rates may nevertheless be important. The on-line pH technique in a dispersed phase configuration may be a quick experimental way of establishing this information.

3.3. Polymer and film properties

Fig. 10(a) and (b) shows the effect of initial monomer mole ratio \((R)\) on the intrinsic viscosity of the polymer formed at different phase volume ratios, respectively for cyclohexane and CCl₄. In both cases and for all the phase volume ratios used, a general feature of the variation can be noticed that, as \(R\) is increased, there is an initial increase in molecular weight of the polymer, attainment of a maximum at a value of \(R\) somewhat greater than 1.0, followed by a gradual decrease. Broadly speaking, the trends are similar to what has been reported in the literature [7]. In melt polycondensation, a strict equivalence of functional groups is what is required for attainment of high molecular weights, the latter falling off rapidly as one deviates from a mole ratio of 1. With IP, if one takes the reaction to occur in a thin zone on the organic side of the interface, the situation is more like a semibatch reactor, with the aqueous phase monomer supplied continuously by diffusion to the reaction zone, which has an excess of the organic phase monomer. The molecular weight results are consistent with the trends observed in kinetics, where it was found that there was effectively an excess of amine with a mole ratio of 1; apparently a value of \(R\) higher than 1 is needed to achieve effective molar equivalence in the reaction zone.

While the phase volume ratio was seen to influence the kinetics (Fig. 6), Fig. 10 shows that its influence is slight on molecular weight. While a large influence is seen at \(R = 1\) for cyclohexane, this seems to be more an aberration than representative of the general trend. As to the effect of solvent, while the trends are very similar, in general the molecular weights seem to be larger with CCl₄ than with cyclohexane. This is likely to be because CCl₄ is a better solvent for the polyurea oligomers than cyclohexane. The oligomers therefore stay and grow for longer times in the former solvent as compared to cyclohexane.

Fig. 10. Variation of intrinsic viscosity (molecular weight) of the polymer formed, with the monomer mole ratio used (a) cyclohexane as solvent and (b) CCl₄ as solvent.
Table 4
Intrinsic viscosity and crystallinity of the samples with different \( n_L/V_d \).

<table>
<thead>
<tr>
<th>System</th>
<th>Run</th>
<th>( n_L/V_d )</th>
<th>( V_d/V_c )</th>
<th>( R )</th>
<th>[( \eta )] (dl/g)</th>
<th>( X_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water–cyclohexane</td>
<td>S32</td>
<td>0.188</td>
<td>0.25</td>
<td>5</td>
<td>0.2865</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>S48</td>
<td>0.24</td>
<td>0.25</td>
<td>5</td>
<td>0.2857</td>
<td>0.32</td>
</tr>
<tr>
<td>Water–CCl4</td>
<td>T14</td>
<td>2.0</td>
<td>0.1</td>
<td>0.8</td>
<td>0.3872</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>T15</td>
<td>0.5</td>
<td>0.1</td>
<td>0.8</td>
<td>0.3826</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Table 4 shows a comparison between two experiments with different values of \((n_L/V_d)\) for the two solvents. As in the case of kinetics, this parameter is seen to have a negligible influence on molecular weight. In summary therefore, it appears that the mole ratio of monomers is the most important determinant of the molecular weight achieved.

The behavior of the polymer samples in DSC shows some interesting features. Figs. 11–14 show DSC scans of some representative samples. A DSC scan for sample S6 is shown in Fig. 11. Polyurea is a high melting thermoplastic [5], with a melting temperature of about 285 °C. Fig. 11(a) shows an exothermic peak at a temperature just below melting, at about 250 °C. As observed in our earlier work [5], this peak represents a cold crystalline transition, as the polymer

![Fig. 11. DSC scan of sample S6 (R = 1.25, \( n_L/V_d = 0.48 \) and \( V_d/V_c = 0.045 \)).](image1)

![Fig. 12. DSC scan of sample S15 (R = 2, \( n_L/V_d = 1.5 \) and \( V_d/V_c = 0.045 \)).](image2)

![Fig. 13. DSC scan of sample S16 (R = 3, \( n_L/V_d = 1 \) and \( V_d/V_c = 0.045 \)).](image3)

![Fig. 14. DSC scan of sample T21 (R = 2, \( n_L/V_d = 0.6 \) and \( V_d/V_c = 0.25 \)).](image4)
chains arrange themselves into the maximally ordered structure under the conditions of increased mobility. Thus when this sample is allowed to cool and the DSC run again (Fig. 11(b) shows the re-run); the exothermic peak is no longer seen. In some samples, there is also a suggestion of small endothermic peak just below the melting point (see Figs. 12–14), which could be the melting of imperfect crystals formed during polymerization. The endothermic peak was more conspicuous in cases where CCl₄ was the solvent, as in the case of T21. These results suggest that the polymer is not allowed to realize the maximum crystalline order it is capable of, under the conditions of polymerization. This fact is of some importance in applications which depend on permeation of molecules through the polymer film, since crystallinity can lower permeation rates considerably.

Fig. 15 shows the XRD of the sample S6 (whose DSC was discussed above) as formed. A semi-crystalline nature is apparent, and all the samples showed prominent crystalline peaks in the region 10° < 2θ < 30°. A degree of crystallinity (Xₚ) can be calculated [5,30–32] by drawing an amorphous halo and comparing the area under the crystalline peaks to the total area under the crystalline peaks and amorphous halo. Crystallinities of samples prepared under identical conditions (repeat runs, T14 and T15) along with that of other samples are shown in Table 4. The maximum crystallinity, as calculated by the method described in the literature [33], was found to be about 0.5.

The ease of crystallization for a given solvent, apart from thermodynamic considerations such as solubility, would be a function of other variables such as chain length, which as intrinsic viscosity data indicate, in turn depend on preparation conditions. Goyal and Suresh [16] and Yadav et al. [5], from results with cyclohexane as an organic solvent, speculated that conditions which result in a high rate of polymerization would produce polymer with a lower degree of crystallinity, as the polymer grows and comes out of solution faster than the molecules can arrange in crystalline order. In the present work, in addition to the water–cyclohexane system, water–CCl₄ system has also been used. Values of crystallinity obtained in the present work and reported have been plotted against the product of initial monomer concentrations used in the syntheses as shown in Fig. 16(a) and (b) for cyclohexane and CCl₄ respectively. The product of initial concentrations can be taken as a measure of the initial rate of reaction.

It is seen that there does exist a rough correlation between the rate of reaction and the crystallinity of the polymer, the correlation being more noticeable in the case of CCl₄ than cyclohexane. Clearly however, the interplay of several factors needs to be taken into account in order to properly account for the variation of polymer crystallinity with synthesis conditions. This is best done through a model that accounts for the different rate and equilibrium processes that are important in polymer formation, phase separation and crystallization.

4. Conclusions

An experimental study of IP to produce polyurea microcapsules has been carried out in this work, with a view to gaining insights into the kinetics and film properties in such a process. The process is complex, involving multiphase transport processes, multi-step kinetics and the kinetics and thermodynamics of phase separation of the formed polymer. The reaction conditions have been varied through three experimental parameters, namely, the initial mole ratio of monomers, R, the phase volume ratio, V_d/V_c, and the moles of limiting monomer per unit volume of the dispersed phase, n_l/V_d. A variety of solvents have been employed for the organic phase monomer in order to elucidate the effect of solvent on reaction kinetics. The results show that the reaction proceeds under kinetic
control for most of the conversion range provided the films formed are sufficiently thin. The reaction rate, under identical values of the process parameters chosen, depends on the solvent used, which indicates that the reaction occurs on the solvent-side of the interface. Contrary to expectations, the rate constants do not correlate with the partition coefficient of HMDA in the solvent; solvent polarity seems to be the more important determinant of reaction rate. The polymer formed is of low molecular weight, the molecular weight peaking when encapsulation is carried out with a mole ratio R slightly in excess of 1. The polymer is semi-crystalline, and the actual crystallinity of the as-formed polymer depends on prepa-
rations conditions. A rough inverse correlation between the rate of polymerization and crystallinity has been found, with conditions that promote a high rate of reaction leading to low crystallinity in the film. However, crystallinity seems to depend on other factors also, which in turn may depend on reaction kinetics in a complex manner.

While microencapsulation is of interest in its own right, this work shows that it also provides a convenient method of studying IP's in general, since self-supporting membranes can be formed in this method. The on-line pH technique has been shown to be a convenient technique to study the reaction. The conclusions arrived at are of broad applicability to other processes that depend on this technique, such as production of thin film composite membranes, and provide valuable inputs on the basis of which mathematical models of the process can be developed.

References


Greek letters
\(\alpha_s\) Swelling index, volume ratio of swollen polymer to dry polymer
\(\rho_p\) Polymer density (kg/m\(^3\))
\(\delta_m\) Maximum possible film thickness (m)
\([\eta]\) Intrinsic viscosity (dl/g)

Subscripts
0 Initial state
A HMDA
B HMDI
c Continuous phase
d Dispersed phase

Nomenclature
\(a\) Interfacial area per unit volume (m\(^{-1}\))
\(CA\) HMDA concentration (kmol/m\(^3\))
\(CB\) HMDI concentration (kmol/m\(^3\))
\(dp\) Microcapsule diameter (m)
\(h, h_0\) Hydrogen ion concentration (kmol/m\(^3\))
\(MA, MB\) Molecular weights of HMDA and HMDI (kg/kmol)
\(n_L\) Number of moles of limiting monomer (kmol)
\(R\) Bulk molar ratio of reactants
\(V\) Volume (m\(^3\))
\(X\) Fraction conversion
\(X_c\) Crystallinity