

# Effect of various parameters on formation of polyurea microcapsules by interfacial polycondensation techniques.

K. T. Jadhav, P. V. Vijay Babu

Department of Chemical Engg. D. Y. Patil College of Engg. & Tech., Kolhapur, Maharashtra, 416 006, India  
Department of Chemical Engg. Dr. B. A. T. University, Lonere, Maharashtra, 402 103, India

## Abstract

Interfacial polycondensation is one of the effective methods used for the rapid production of polymers at a smaller scale. Interfacial polycondensation has been studied for various applications such as synthesis of polymers, production of thin film composite membrane, micro encapsulation, etc. In these reactions, the reactants are brought together at an interface of two immiscible phases. An Interfacial reaction provides the possibility of fast reactions with production of low molecular weight polymers under ambient conditions. This is an important technique in the formation of polyurea microcapsules. The formation of aqueous core polyurea microcapsules via interfacial polycondensation of a Toluene Diisocyanate (TDI) in organic solvent and Ethylene Diamine (EDA) in water is studied. The formed microcapsules are insoluble in both the phases. Detailed kinetic information has been obtained by using a continuous pH measurement system. The polymer formed is thermoplastic and semi crystalline in nature which having melting point of about 295°C. It is generally assumed that the reaction is second order and rate of reaction is diffusion controlled. The aim of this work was to determine the optimum conditions which are useful for the formation and enhancing properties of microcapsules by optimizing various parameters such as stirring speed, solvent proportion, monomer ratio, surfactant concentration and pH of the aqueous phase. Crystallinity of polyurea microcapsules were studied by X ray Diffraction (XRD) method.

**Keywords:** Interfacial polycondensation, microcapsules, thermoplastic, crystallinity, kinetics, diffusion controlled.

## 1. Introduction

Interfacial polycondensation reactions, in which reactants (monomers) are brought together at interface between two immiscible phases, and formed microcapsules near the interface in organic side. It came into existence in the 1950s with the work of Morgan, Wittbecker and co-workers on polyurethanes, polyamides and other polymer classes. Polyurea microcapsule finds various applications in microencapsulation, synthesis of polymers, composite membrane, fibres and coatings. This method is useful for polymers which are thermally unstable and for the polymers having reactive functional groups. Hundreds of polymers have been made by this process. Polycarbonates and aromatic polyamides are reported to be prepared commercially by stirred interfacial polycondensation technique [4, 10, 19].

In this interfacial reactions TDI in organic solvent bring in contact with an aqueous solution of an EDA, stirring the mixture vigorously, and separating the microcapsules. Various equilibrium physicochemical processes involved are ionic equilibrium for EDA, transport of EDA and/or TDI from bulk phase to reaction interface, reaction between these two monomers and finally phase separation of microcapsule species [20]. The performance of these

microcapsules depends upon its chemical composition and properties such as thickness, crystallinity, molecular weight, mechanical and thermal properties etc [8, 12].

## 2. Experimental studies

Toluene Diisocyanate (TDI) of purity above 99% and Ethylene Diamine (EDA) of purity above 98% were both obtained from Fluka, Switzerland, and used without further purification. Solvents and other chemicals used in the preparation of samples were of analytical grade. Distilled water was used as the solvent for EDA. The surfactant Tween-85 obtained from Fluka, Switzerland and Sodium Lignosulfonate also was used to stabilize the oil in water emulsion. Methanol is used to remove unreacted monomers during washing of microcapsules. The experimental procedure for the preparation of polyurea microcapsules was similar to that followed earlier by Yadav, A. K. Suresh & Wagh, [11, 13, 14]. A two step procedure is carried out as follows for the preparation of polyurea under given conditions. In the first step, oil in water emulsion is prepared by using Toluene Diisocyanate (TDI), cyclohexane, Tween 85 as a surfactant (2 to 4 % v/v of distilled water) and distilled water (oil : water = 1:2 vol/vol). The emulsification was carried out in a beaker for 15 minutes by stirring at

speed of approximately 3000 rpm with four bladed pitched turbine impeller (Remi Motors Ltd. Model with

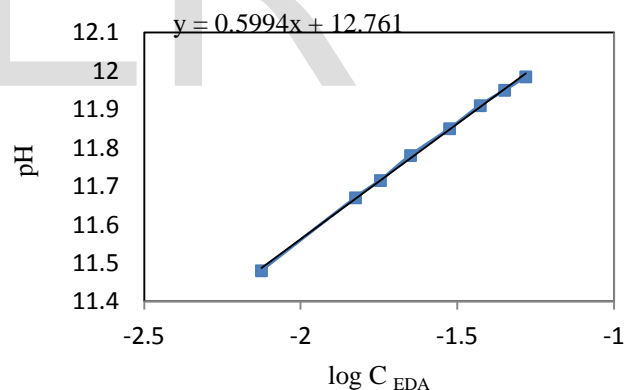
a 1 hp motor). By keeping the above conditions fixed, similar procedure has followed for all experiments to obtain same emulsion drop size distribution [14].

In the second step, the required amount of this emulsion (depending on ratio of dispersed phase to continuous phase i.e. phase volume ratio) was added to a beaker containing aqueous solution of EDA. The beaker consist a thermometer and a pH probe, connected through a pH-meter for the pH and conversion measurement. Thus initiating the polycondensation reaction between EDA and TDI. The reaction mixture kept agitating using a magnetic stirrer. pH is measured on line to study conversion of product and for data collection [13, 14]. The reaction leads to the formation of polyurea microcapsules at the interface. After that stirring is stopped and the final product formed is taken out from the beaker. The product is then washed with warm distilled water and methanol alternatively for 3-4 times to remove unreacted monomers and dried with the help of filter paper. The product is then sent to dryer for constant temperature of 60°C, and then the product obtained is sent for different analysis. Characterizations of microcapsules are important to know about physical and chemical properties. Samples of polyurea for various characterization studies were prepared and some of the dried sample was preserved for SEM, XRD, DSC and FTIR analysis [3, 20].

In this work, different parameters have been considered by carrying out a set of experiments. These parameters are monomer mole ratio (R), phase volume ratio ( $V_d/V_c$ ) and number of moles of limiting monomer per unit volume of dispersed phase ( $N/V_d$ ). Experiments were conducted for three different values of the phase volume ratio ( $V_d/V_c$ ) are 0.10, 0.25 and 0.50. At each phase volume ratio, mole ratio of the monomers is varied from 4 to 12 and  $N/V_d$  is varied between 0.3 to 0.6. The monomer mole ratio of is an important parameter to control the molecular weight and  $N/V_d$  is used to controls the film thickness. The concentrations of EDA used were such that change in pH is in given range [11]. The reproducibility of the experiments was checked by repeating some runs completely. In such experimental runs, the reproducibility of the characterization of samples was also done by conducting few analysis steps (i.e. FTIR and XRD analysis) separately.

## 2.1 Calibration of pH of diamine solution as a function of concentration

Ethylene Diamine is highly alkaline in a nature. Addition of EDA into TDI solution decrease pH of reaction mixture drastically from 12.5 to 7. The reaction ends when the pH value becomes nearly constant. Then agitation of reaction mixture was stopped and the microcapsules were filtered out. Calibrations of pH of diamine solutions are essential as this is function of concentration of EDA. Relationship of pH of solution to concentration of EDA gives a straight line which has been shown in earlier work [11]. An accurate measurement of the pH is essential for getting data of reaction kinetics. The surface of pH probe must be clean during the experiments. The size distribution of capsules was determined for few selected experiments in a particle size analyser. All reactions are carried out at ambient conditions. The emulsion formed in the first step of the experimental procedure was having a sufficient stability so that the drop size distribution remained constant throughout the reaction. Fig. (1) shows a relation of pH as function of concentration of diamine solution.



**Fig. (1):** Calibration plot of pH of solution to concentration of EDA

In earlier work [14] this relationship is expressed by the following rate equation,

$$C_A = k \cdot H^{-c} \quad \dots\dots (1)$$

Where,

$C_A$  is the concentration of EDA.

$H$  is hydrogen ion concentration.

$k$  is rate constant

$c$  is constant whose value lies in the range of 1.50 – 1.70.

## 2.2 Determination of partition coefficient of solvents in EDA

To study the effect of the solvent for the organic phase monomer on reaction kinetics and properties, cyclohexane was used as solvent for TDI. The partition coefficient of the various solvents into the ethylene diamine solution in determining the kinetics is explained in the literature [9, 18]. Some experiments were also conducted with toluene, benzene and p-xylene to study various aspects of kinetics. The aqueous and organic phases, separated from shake flask after equilibration, were titrated against HCl and methyl orange is used as an indicator to obtain the concentrations. It has found that cyclohexane has highest partition coefficient value than the other solvents. So, cyclohexane is used as a solvent for remaining experimentation.

## 3. Results and discussion

Effects of various parameters are studied to obtain optimum conditions which allow formation of polyurea microcapsules. The whole the system was studied by considering various parameters which includes pH of the aqueous phases, solvent proportion, monomer ratio and phase volume ratio [9]. Some of the important parameters affecting on the rate of interfacial polycondensation are as follows.

### 3.1 Effect of pH and conversion with time

Reaction rate of the reaction is important factor in case of interfacial polycondensation reactions. Stirred interfacial method requires the fast reacting monomers and the rate of reaction is considerably greater than the method without stirring. The values of reaction rate for the faster reactions are estimated of the order of  $10^2$ - $10^6$  lit/mol.sec [11].

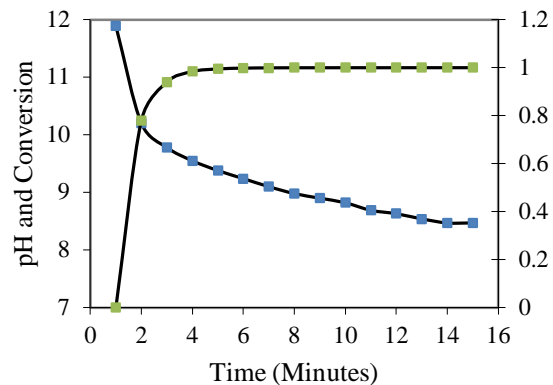


Fig. (2): Graph of pH and conversion with respect to time ( $R = 10$ ,  $N/Vd = 05 \text{ kmol/m}^3$  and  $Vd/Vc = 0.25$ )

Fig.(2) shows a graph for change in pH and diamine conversion with respect to time. The experiment has carried out using cyclohexane as the solvent for TDI with monomer mole ratio of 10. The conversion of amine is above 95%, so that most of the reaction is completed in 5 minutes. EDA being the limiting monomer, its pH value is reached to 7.0, indicating total consumption of amine. The reaction ends when the pH value becomes nearly constant. Then agitation of reaction mixture was stopped.

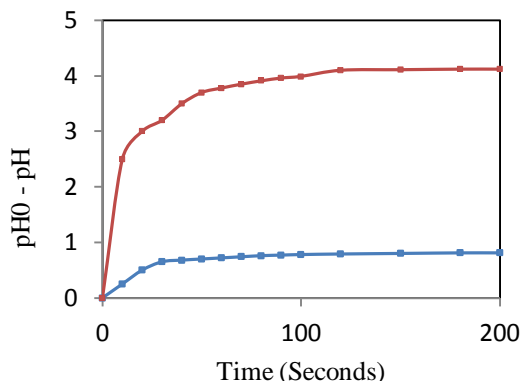
$$X = 1 - \left(\frac{h}{h_0}\right)^{-C} = 1 - 10^{-(pH_0 - pH)C} \text{ ----- (2)}$$

Eq. (2) gives the rates of the reaction under various conditions [5, 11].

### 3.2. Effect on monomer mole ratio on kinetics of reaction

Fig.(3) shows the rates of reaction for two experiments on this basis, the experimental conditions being identical except for the value of  $R$ , which is 4 for one experiment (S18) and 8 for the other (S21). For  $R = 4$ , we would expect both monomers to be consumed completely, but the result in Fig. (3) indicates that the amine is not completely consumed, the conversion at the end of the reaction being about 80% where as for  $R$

= 10, conversion has reached to more than 99 %.



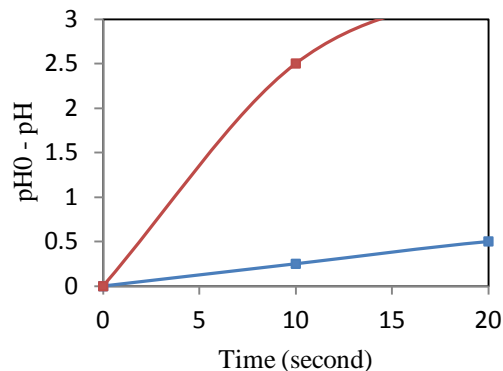
**Fig. (3):** The effect on monomer mole ratio on kinetics of reaction ( $R = 4$  and  $R = 10$ ), other parameters are same ( $N/V_d = 0.6 \text{ kmol/m}^3$ ,  $V_d/V_c = 0.25$ ).

Three types of oligomers are expected to form in such step 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 behaviour 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 therefore a complete consumption of the diisocyanate monomer took place before the diamine. This reaction is likely to be taken place on the organic side of the interface [11, 16].

A differentiation equation (1), gives the following relation between the rate of consumption of monomer A, concentration and the rate of decrease of pH as,

$$\left(\frac{1}{c_A}\right) \frac{dc_A}{dt} = 2.3026 C \frac{dpH}{dt} \quad \text{----- (3)}$$

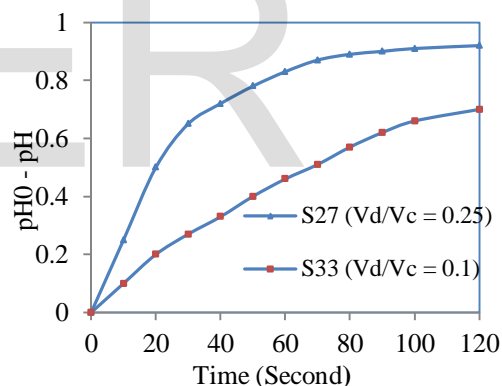
The initial part of the pH vs. time curves for the experiments shown in Fig. (3) are replotted in Fig. (4), which show the linear relationship. In experiment S18 conversion goes up to 80 %, and, in the case of S21, it goes up to 99%. From equation (3) the overall proportionality of the rate to the concentration of A over a wide range of conversion. The two experiments were conducted with same initial concentrations of the ethylene diamine, but with different diisocyanate concentrations. The considerable influence of the diisocyanate concentration on the rate is indication of the reaction is taking place to the organic side.



**Fig.(4):** pH vs. time data for the initial time of experiment. The best fit straight lines have slope of 0.086 for S18 and 0.0216 for S21.

### 3.4. Effect of phase volume ratio on kinetics of reaction

Fig.(5) shows the effect of phase volume ratio on the kinetics of the reaction. As the phase volume ratio influences the interfacial area as well as the initial concentration of EDA, both of which are higher for the case of S27. The runs shown in the figure (5) are for the monomer ratios 9.0.



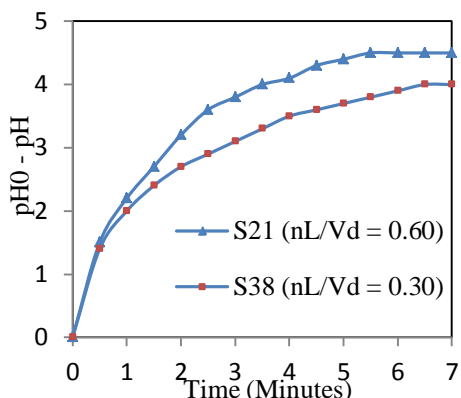
**Fig.(5):** Effect of phase volume ratio on the kinetics, other conditions being identical ( $R = 9.0$ ,  $N/V_d = 0.6 \text{ kmol/m}^3$ )

The variation in the concentration of A during the experiment has an influence on the kinetics in this case, which has shown in the profile [9]. The final conversion achieved in both cases was the same. The interfacial character of the reaction is clear from the substantial influence on the interfacial area in the fig. (5).

### 3.5. Effect of $N/V_d$ ratio on kinetics of reaction

Fig.(6) shows the effect of  $N/V_d$  on process kinetics. The moles of limiting monomer restrict the amount of polymer that is formed, and this ratio therefore determines the final film thickness. The experiments

being were conducted under same values of the other parameters, but because of the difference (by a factor of 2) in the number of moles of limiting monomer (EDA in this case), differ in the final thickness of the film.



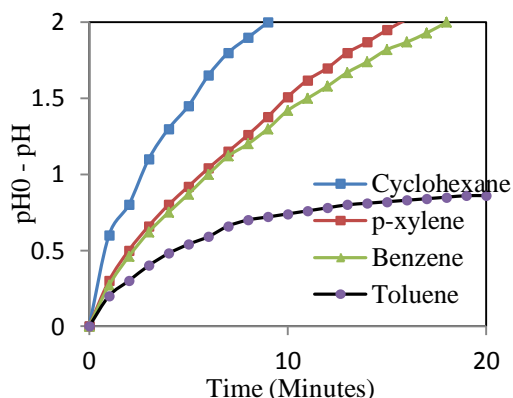
**Fig.(6):** Effect of  $N/Vd$  on process kinetics (other conditions are same,  $R = 8.0$  and  $Vd/Vc = 0.25$ ).

The smaller  $N/Vd$  exhibiting a higher rate towards the end of reaction. It is possible that diffusion limitations are responsible for lowering the rate in the case of the

thicker film [11, 13]. The results indicate that in the Fig. (6).Influence of the parameter  $N/Vd$ , which determines the final film thickness, on kinetics (other conditions  $R = 8.0$  and  $Vd/Vc = 0.25$ ).limitations become important only towards the very end under these conditions. In other similar sets of experiments where the differences in  $N/Vd$  were smaller (say 30 - 40%), the kinetics were virtually reproduced over the entire range of pH.

### 3.6. Effect of solvent on kinetics of reaction

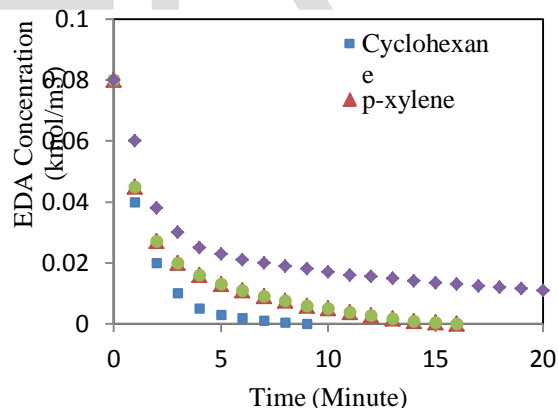
Fig.(7) shows the change in  $pH_0 - pH$  values for various solvents (for organic phase monomer) with time.The rate is seen to be higher for cyclohexane than other solvents in all cases.



**Fig.(7):**Solvent effect on reaction kinetics: variation of  $(pH_0 - pH)$  with time for four different solvents ( $N/Vd = 0.6$ ,  $R = 10$  and  $Vd/Vc = 0.25$ ).

Fig.(8) shows effect of solvents on reaction kinetics.The selection of the organic solvent is one of the important parameter since it affect several other factors such as the partition coefficient of the reactants between the two phases, the diffusion of the reactants, reaction rate, and the solubility of polymer. Partition coefficients of various solvents are experimentally studied. The common organic solvents which are inert and immiscible with water are generally preferred in interfacial polycondensation systems. Aromatic and chlorinated hydrocarbons are particularly useful.

Some experiments are conducted in various solvents to study certain aspects of process kinetics. Many experiments have been carried with various solvents like Cyclohexane, p-Xylene, Toluene and benzene. We found that Cyclohexane is the best suitable solvent for TDI and EDA system [5, 6, 17]. Since a choice of solvents is available for applications such as the manufacture of thin film composite membranes, 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.



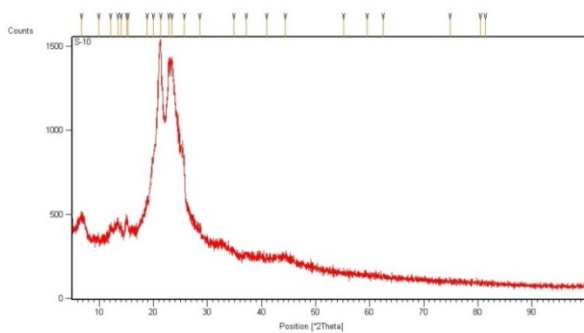
**Fig.(8):** Effect of solvents on reaction kinetics: EDA concentration vs. Time for four different solvents ( $R = 8.0$ ,  $Vd/Vc = 0.25$ ,  $N/Vd = 0.6$ )

### 3.7. XRD Analysis of polyurea samples

X-ray diffraction (XRD) is a useful technique that provides detailed information about the chemical composition and crystalline structure of materials. The information obtained from the scattering at wide angles described the spatial arrangements of the atoms.

Low-angle x-ray scattering is useful in detecting larger periodicities. Therefore x-ray method is used to determine the crystal structures of polymers. The powder X-ray diffraction (XRD) patterns of the polymer samples were measured in the reflection mode on a wide angle X-ray. Fig.(9) shows the XRD of the samples S10. A semi-crystalline nature is shown and all the samples showed crystalline peaks lies in the region  $20^\circ < \theta < 30^\circ$ . A degree of crystallinity ( $X_c$ ) can be calculated by drawing an amorphous halo and comparing the area under the crystalline peaks to the total area under the crystalline peaks and amorphous halo [15]. The maximum crystallinity, as calculated by the method described in the literature [1], was found to be about 0.5. The ease of crystallization for a given solvent, apart from thermodynamic considerations such as solubility, would be functions of other variables such as chain length, which as intrinsic viscosity data indicate, in turn depend on preparation conditions. Goyal and Suresh [7] and Yadav et al. [12], from results with cyclohexane as an organic solvent, showed 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 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. (9) for cyclohexane as solvent. 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.



**Fig.(9):** XRD diffractogram of sample S10  
( $V_d/V_c = 0.25$ ,  $R = 9.0$ ,  $N = 0.045$  moles)

#### 4. Conclusions

In this paper, we have discussed effect of the various reaction parameters on the kinetics of formation of polyurea microcapsules. Polyurea microcapsules were prepared by interfacial polycondensation reaction between Toluene Diisocyanates and Ethylene Diamine to study the effects of the chemical structure on various characteristics. The reaction conditions have been studied by changing a various parameters, such as the monomer ratio,  $R$ , the phase volume ratio,  $V_d/V_c$  and the moles of limiting monomer per unit volume of the dispersed phase,  $N/V_d$ . It is observed that reaction rate is important parameter in formation of polyurea microcapsules. Addition of EDA into TDI solution decrease pH of reaction mixture drastically from 12.5 to 7. The reaction ends when the pH value becomes nearly constant. It has found that cyclohexane has highest partition coefficient value than the other solvents. It is found that when monomer ratio increases up to 10, we get better results. The moles of limiting monomer limit the amount of polymer that is formed, and this ratio therefore determines the final film thickness of polymer formed. Phase volume ratio influences the interfacial area as well as the initial concentration of EDA. The suspensions of polyurea microcapsules were most stable when EDA monomer was used. Low crystallinity of the microcapsules is essential for the growth of microcapsules. XRD results prominently showed a semi crystalline nature and a peak lies in given range which showed that polyurea microcapsules are successful prepared.

#### Nomenclature

- $a$  - Interfacial area per unit volume ( $m^{-1}$ )
- $C_A$  - EDA concentration ( $kmol/m^3$ )
- $C_B$  - TDI concentration ( $kmol/m^3$ )
- $h$  - Hydrogen ion concentration ( $kmol/m^3$ )
- $M_A, M_B$  - Molecular weights of EDA and TDI ( $kg/kmol$ )
- $N$  - Number of moles of limiting monomer ( $kmol$ )
- $R$  - Monomer molar ratio
- $V$  - Volume ( $m^3$ )
- $X$  - Conversion
- $X_c$  - Crystallinity

#### References

- 1) D.W. Van Krevelen, Properties of Polymers Their Estimation and Correlation with Chemical Structure, Elsevier, Amsterdam, 1976.

- 2) E. Jabbari, Morphology and structure of microcapsules prepared by interfacial polycondensation of methylene bis(phenyl isocyanate) with hexamethylenediamine, *Journal of Microencapsulation* 18 (2001) 801.
- 3) F. MacRitchie, Mechanism of interfacial polycondensation, *Transactions of the Faraday Society* 65 (1968) 2503.
- 4) F.W. Billmeyer, *Textbook of Polymer Science*, 2nd edition, Wiley-Interscience, New York, 1971.
- 5) J.B. Ephraim, A.E. Woodward, R.B. Mesrobian, Kinetic studies of the reaction of phenyl isocyanate with alcohols in various solvents, *Journal of the American Chemical Society* 80 (1958) 1326.
- 6) M.C. Chang, S.A. Chen, Kinetics and mechanism of urethane reactions: phenyl isocyanate-alcohol systems, *Journal of Polymer Science, Part A: Polymer Chemistry* 25 (1987) 2543.
- 7) N. Goyal, A.K. Suresh, Kinetics and structure inter-relationships in interfacial polycondensation, in: *Proceedings of the International Conference on Advances in Chemical Engineering*, IIT Madras, Chennai, India, 1996.
- 8) P.W. Morgan, S.L. Kwolek, Interfacial polycondensation. II. Fundamentals of polymer formation at liquid interfaces, *Journal of Applied Polymer Science* 13 (1959) 1741.
- 9) P. Morgan, *Condensation Polymers: by Interfacial and Solution Methods*, Wiley, New York, 1965.
- 10) R. Petersen, Composite reverse osmosis and nanofiltration membranes, *Journal of Membrane Science* 83 (1993) 81.
- 11) S. J. Wagh, S. S. Dhupal, A. K. Suresh, An Experimental study of polyurea membrane formation by interfacial polycondensation, *Journal of Membrane Science*, *Journal of Membrane Science* 328 (2009) 246 – 256.
- 12) S.K. Yadav, N. Ron, D. Chandrasekharam, K.C. Khilar, A.K. Suresh, Polyureas by interfacial polycondensation: preparation and properties, *Journal of Macromolecular Science-Physics* 35 (1996) 807.
- 13) S.K. Yadav, A.K. Suresh, K.C. Khilar, Microencapsulation in polyurea shell by interfacial polycondensation, *AIChE Journal* 36 (1990) 431.
- 14) S.K. Yadav, K.C. Khilar, A.K. Suresh, Microencapsulation in polyurea shell kinetics and film structure, *AIChE Journal* 42 (1996) 2616.
- 15) S.K. Yadav, K.C. Khilar, A.K. Suresh, Release rates from semi-crystalline polymer microcapsules formed by interfacial polycondensation, *Journal of Membrane Science* 125 (1997) 213.
- 16) S.K. Karode, S.S. Kulkarni, A.K. Suresh, R.A. Mashelkar, Molecular weight distribution in interfacial polymerization: model development and verification, *Chemical Engineering Science* 52 (1997) 3243.
- 17) T.J. Hsu, L.J. Lee, Reaction injection molding of polyureas. I. Kinetic study, *Polymer Engineering and Science* 28 (1988) 955.
- 18) T. Kondo, Microcapsules: their preparation and properties, in: E. Matijevic (Ed.), *Surface and Colloid Science*, vol. 10, Plenum, New York, NY, 1978, pp. 1–41.
- 19) T. Kondo, Permeation, Permeability characteristics of microcapsule membranes, *Journal of Controlled Release* 11 (1990) 215.
- 20) S. S. Dhupal, S. J. Wagh, A. K. Suresh, Interfacial polycondensation – Modelling of kinetics & film properties. *Journal of Membrane Science*, 325 (2008) 758-771.