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### Kinetic Studies of Block Polycondensation. I. Aggregation of Various Carboxylic Acids in Solvents of Low Dielectric Constant

Pierre-Jean Madec<sup>a</sup>; Ernest Marechal<sup>b</sup>

<sup>a</sup> Institut National Supérieur de Chimie Industrielle, Mont Saint-Aignan, France <sup>b</sup> Laboratoire de Synthèse, Macromoléculaire Université P. et M. Curie, Paris, France

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## **Kinetic Studies of Block Polycondensation. I. Aggregation of Various Carboxylic Acids in Solvents of Low Dielectric Constant**

**PIERRE-JEAN MADEC**

Institut National Supérieur de Chimie Industrielle  
de Rouen  
BP 8, 76 130 Mont Saint-Aignan, France

and

**ERNEST MARECHAL**

Laboratoire de Synthèse Macromoléculaire  
Université P. et M. Curie  
4 place Jussieu  
75 230 Paris, France

### **ABSTRACT**

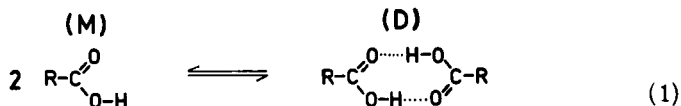
Self-association of benzoic, octanoic, and octadecanoic acids was studied in solvents with a range of dielectric constants between 2.3 and 10. The number-average molecular weights were determined by means of vapor pressure measurements and were carried out at temperatures ranging from 25 to 90°C. It appears that, in these solvents of low dielectric constant, carboxylic acids are present mainly as molecular or ionic aggregates.

### **INTRODUCTION**

In our work on block polycondensation we have studied the kinetics of the reaction of oligomers with epoxy endgroups and oligomers with

carboxylic endgroups. Under our experimental conditions (solvents of low dielectric constant), it appears that the kinetics is largely determined by the self-association of the acidic group and its modification in the presence of the catalyst. This first article is devoted to the study of the aggregation of various carboxylic acids.

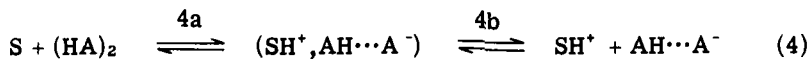
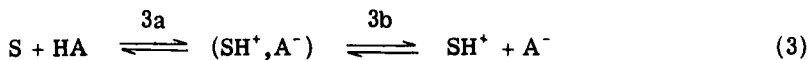
Self-association of carboxylic acids has been largely studied extensively; in nonpolar solvents the dimerization of carboxylic acids is mainly due to hydrogen-bonding according to the scheme (1).



Most of the studies relative to the self-association of carboxylic acids in organic solvents with a low dielectric constant have been carried out around room temperature (25-37°C), which is the most favorable to the existence of the hydrogen bonds involved in dimer D [1-3]. In the present paper the association of carboxylic acids in solvents of low dielectric constant was studied at temperatures well above room temperature with the use of vapor pressure osmometric measurements. Other equilibria than (1) have been described. The solvents have been chosen for the fact that they cover a range of dielectric constants ( $2.3 < \epsilon < 10$ ) which has not been widely studied. They form an intermediate group between low dielectric constant solvents (benzene, cyclohexane, toluene, for instance) [4-6] and solvents with dielectric constants above 10, such as 1,2-dichloroethane [7]. Acid-base reactions in aprotic solvents with low dielectric constants are complicated by the formation of ion pairs and ionic and molecular aggregates. None of these is basic enough to capture the proton of the acid; in these solvents, acid-base reactions are limited to association reactions involving basic and acid solutes:



Dissolving a carboxylic acid into an organic solvent S amounts to considering the equilibria (3) and (4).



Measurements of electrical conductivity of solutions of benzoic, octanoic, and octadecanoic acids in xylene, chlorobenzene, and o-dichlorobenzene in the concentration range between 0.01 and 0.5 M allows us to state that the contribution of free ions is negligible ( $\Lambda < 0.1 \mu\text{S}$ ). Thus dissociation equilibria (3b) and (4b) can be ignored.

This article is the first of a series relative to basic catalysis in the field of polycondensation reactions. The second will be devoted to equilibria involving acids and tertiary amines in the same solvents and in the same range of temperatures.

## EXPERIMENTAL

### Solvents

Solvents used were xylene ( $\epsilon = 2.3$  at  $20^\circ\text{C}$ ), chlorobenzene ( $\epsilon = 5.71$  at  $20^\circ\text{C}$ ), and o-dichlorobenzene ( $\epsilon = 9.93$  at  $25^\circ\text{C}$ ). Magnesium sulfate-dried solvents were distilled through a Hempel column and stored over Molecular Sieves. Purity was ascertained by gas chromatography. Residual water content, determined by Karl Fischer titration, was less than 0.005%.

### Solutes

Octadecane was distilled under vacuum and cholesterol crystallized in hot 95% ethanol. Benzoic acid (Prolabo) and octadecanoic acid (Fluka) were chromatographic grades and used without further purification; octanoic acid (Merck) was distilled under vacuum. The purity of all the acids was followed both by gas chromatography and basic titration and was found to be above 99.8%.

In order to make the plots as clear as possible only two standardization curves are reported in Fig. 1; however the following standards were used: pyren (202.26), benzil (210.23), polyoxyethylene (Waters standard:  $M = 790$ ).

### Instrumentation

Osmometry was carried out by using a Knauer vapor pressure osmometer equipped with thermistors for organic solvents. Two thermistors have been used: from 25 to  $70^\circ\text{C}$  and from 70 to  $130^\circ\text{C}$ .

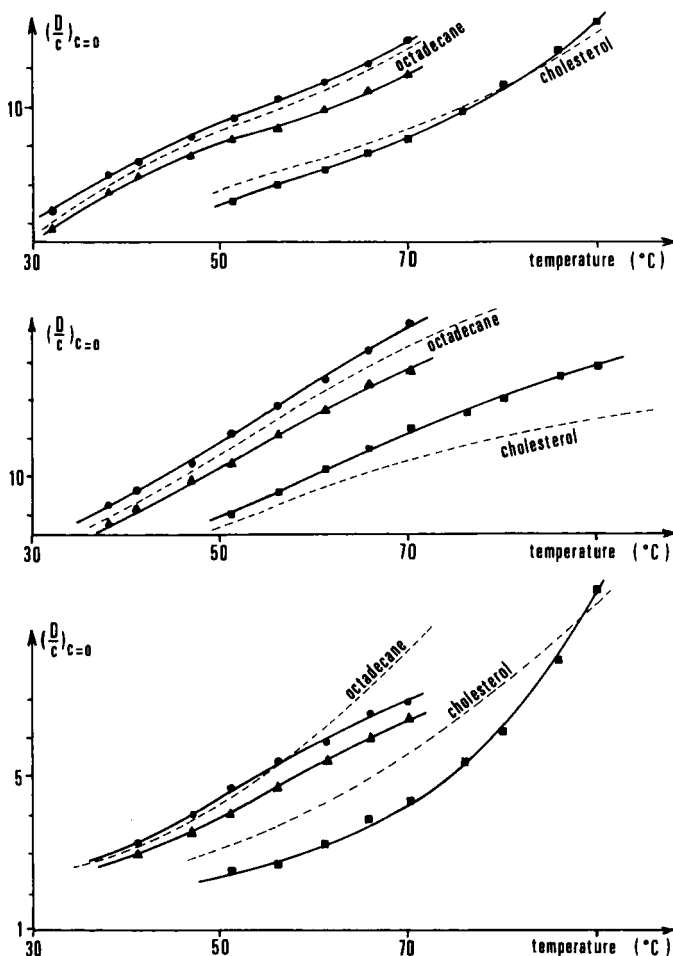


FIG. 1.  $(D/c)_{c=0}$  as a function of temperature for (●) benzoic acid, (▲) octanoic acid, and (■) octadecanoic acid in various solvents: (A) xylene; (B) chlorobenzene; (C) *o*-dichlorobenzene.

### Measurement Techniques

The experiments consist in measuring the equilibrium differential resistance set up between the two thermistors by a drop of solution and a drop of solvent hanging on them. The differential resistance is

recorded on a Wheatstone bridge. If we define  $D$  as the deviation, the number-average molecular weight  $\bar{M}_n$  is related to  $D$  by

$$\bar{M}_n = K/(D/c)_{c=0}$$

where  $c$  is the concentration (g of solute/kg of solvent) and  $K$  a constant obtained by using a standard (st).

$$K = (D/c)_{c=0, \text{st}} M_{\text{st}}$$

The parameters influencing the determination have been examined by various authors [8-10]. According to Morris [10], the vapor pressure of the solute must be less than 0.2 Torr at the temperature of the determination; consequently, the temperatures have been kept below the following limits for various solutes octadecane, 90°C; cholesterol, > 150°C; benzoic acid, 75°C; octanoic acid, 70°C; octadecanoic acid, 148°C.

After hanging a drop of solution on the thermistor, the voltage unbalance is recorded as a function of time, and, according to the authors quoted above, the linear region is extrapolated back to the time when solution is added ( $t = 0$ ).  $D$  is the difference between the baseline and the intersection of the extrapolated line with  $t = 0$ , existing due to the difference in solution and solvent vapor pressures.

Solutions were prepared by weight;  $c$  was in the range 0.005  $\underline{M}$  <  $c$  < 0.5  $\underline{M}$ .

## RESULTS AND DISCUSSION

The values of  $(D/c)_{c=0}$  relative to the standards and benzoic, octanoic and octadecanoic acids are plotted against temperature in Fig. 1; from these curves the values of  $\bar{M}_n$  in various solvents and at various temperatures can be obtained for benzoic, octanoic, and octadecanoic acids.

$\bar{M}_n$  of benzoic and octanoic acids increases slightly with increasing temperature (Figs. 2A and 2B) but stays at about the molecular weight of the dimer. However, when the solvent is *o*-dichlorobenzene,  $\bar{M}_n$  increases greatly when the temperature is above 50°C. This proves that associated species above the dimer are present in the solution. When the temperature is below 50°C, the values of  $\bar{M}_n$  depend to a very small degree on the solvent.

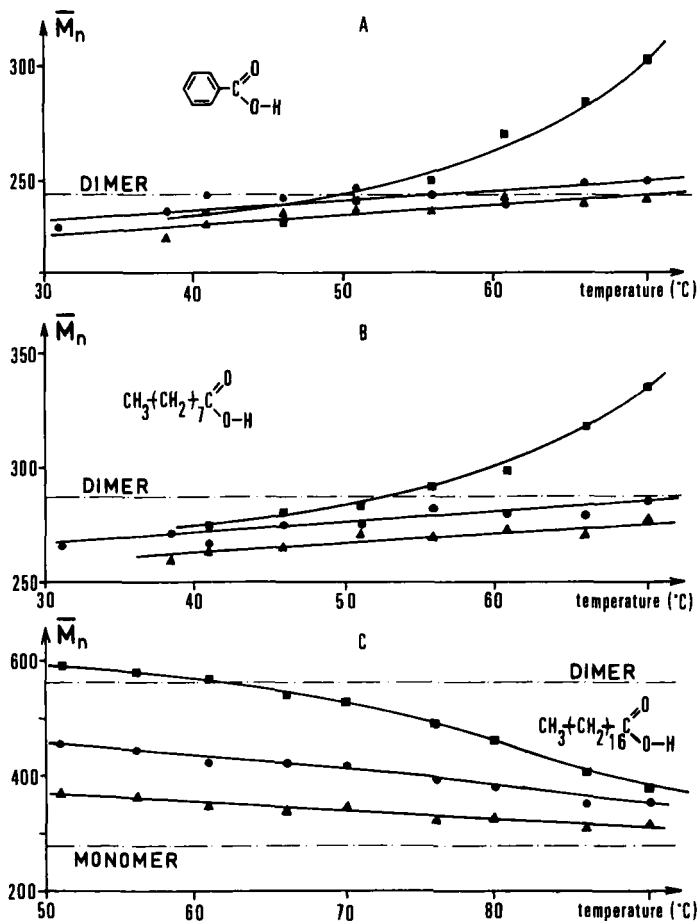
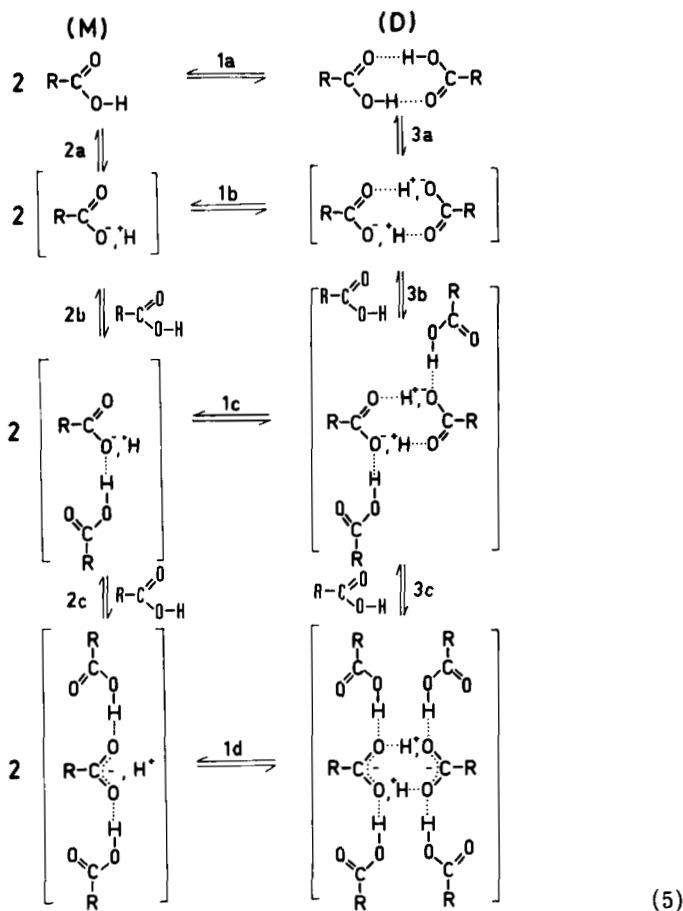


FIG. 2. Variations of the number-average molecular weight ( $\bar{M}_n$ ) with respect to the temperature for (A) benzoic acid, (B) octanoic acid, and (C) octadecanoic acid in various solvents: (●) xylene; (▲) chlorobenzene; (■) o-dichlorobenzene.

$\bar{M}_n$  for octadecanoic acid decreases slowly with increasing temperature (Fig. 2C) and stays between the values for dimer and monomer. The tendency towards association is wider in o-dichlorobenzene than in other solvents and in xylene than in chlorobenzene.

It is clear that equilibrium (1) is not sufficient to explain the observations, and especially the fact that for benzoic and octanoic

acids  $\bar{M}_n$  increases with temperature and that the highest molecular weights are obtained in the most polar solvent. As a consequence, it is reasonable to admit that other equilibria than (1) can exist; they involve associations of ions. The equilibria, which can be reasonably considered for RCOOH, with R aliphatic or aromatic, are reported in Eqs. (5). It appears that monomer (M) and dimer (D) participate



in dissociation equilibria into ion pairs (2a and 3a) and in association equilibria between ion pairs and M (2b, 3b, 2c, 3c). Associations are patently not favored in the case of octadecanoic acid. However for all the acids we studied the strongest associations are observed in



o-dichlorobenzene owing to its higher dielectric constant which is favorable to equilibria (2a) and (3a). In the same way, associations with an intermediate strength could be expected in chlorobenzene; however it can be seen (Fig. 2C) that, in the case of octadecanoic acid, the contribution of associated species is more important in xylene than in chlorobenzene. In fact, both polarizability and the electron-donating power of chlorobenzene are below those of xylene, and solvation of the ion pair is less efficient in the first solvent than in the second. On the other hand, in the case of o-dichlorobenzene, the influence of the dielectric constant prevails over the solvation.

In conclusion, it can be said that in low dielectric constant solvents carboxylic acids are mainly present as molecular or ionic aggregates. This means that in the case of aprotic solvents with a low solvating power towards anion  $A^-$  the solvating agent is HA; consequently the main species are  $(A^-, H^+)_2$  and  $(H^+, AHA^-)$ , which is in agreement with a number-average molecular weight around that of the dimer in the case of benzoic and octanoic acids.

Moreover it appears that differential vapor pressure measurements are particularly suitable for this kind of study, since they provide the number-average molecular weights of the species present in the solution and consequently their degree of association. Moreover, contrary to other methods (cryoscopy, ebulliometry) they allow us to work in a large temperature range.

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