1 Introduction

1.1 Problem Formulation

Polyethylene terephthalate (PET) stands out as a showcase for recycling within the realm of plastics, notably with its widely recognized PET bottle recycling initiatives. As of 2020, approximately 97% of all PET usage, excluding PET fibres, was allocated to the packaging sector in Europe. Within this market, bottles accounted for 70% while trays comprised 20%. Despite the sizable volume of 4.6 million tonnes of rigid PET packaging, only 49% was collected and sorted for recycling in 2020.[1] However, despite these encouraging collection figures, the actual recycled content in PET bottles reached only 17% by the same year. Simultaneously, there has been a growing demand from both industries and consumers for high-quality recycled PET (rPET).[2] Additionally, out of the total PET recycling input, only 54% exits recycling facilities as rPET suitable for high-viscosity applications, and a mere 27% of this is approved for food contact.[1]

To increase these rates, the European Parliament has passed its directive on single use plastics, which among other things, obliges manufacturers to use at least 25 % of rPET in new bottles.[3]

In addition to enhancing collection and sorting methods to bolster the supply and quality of rPET, mechanical recycling faces significant challenges.[1] Apart from dealing with contaminated input streams, the thermal and chemical degradation of PET polymer during reprocessing limits its mechanical recyclability.[4] On one hand, the tensile strength of rPET diminishes with each cycle due to polymer chain scission.[5] Conversely, the polymer's colour darkens and becomes more yellow with increasing recycled content. Furthermore, additives and the inclusion of foreign polymers can substantially alter its properties, thereby limiting its reusability.[6–8] Consequently, new technologies for PET recycling are necessary to overcome these challenges and utilise yet unrecyclable PET waste as a valuable resource.

Back-to-monomer recycling (BMR) emerges as a promising approach under current investigation to restore the properties of virgin PET from previously unrecyclable PET feedstocks such as brittle bottles, multi-layered trays, or even synthetic polyester fibres. While various reaction pathways like alcoholysis, aminolysis, or hydrolysis are being explored, these technologies share a common goal of breaking down PET into its fundamental monomeric building blocks. This targeted depolymerization process liberates contaminants, colorants, and other by-products that can subsequently be treated and removed.[9]

Among these, the approaches using hydrolysis are of special interest as they produce terephthalic acid (TA) and ethylene glycol (EG), the reactants for direct esterification to PET.[10,11] Since TA is practically insoluble in water, it remains as solid after neutral and acidic hydrolysis making it practically impossible to be separated from the reaction residue.[12] While this can be overcome through mixing in alkaline solution leading to the respective alkali salt of TA, this step can be skipped by directly using alkaline hydrolysis. Biermann and Brepohl et al. depolymerized a PET dual layer in less than one minute and up 97 % yield by using sodium hydroxide.[13,14] The EG and TA precursor disodium terephthalate (DST) were dissolved in water and underwent filtration for solids removal.

However, regardless of the depolymerization pathway, the consecutive recovery of TA from DST demands sodium replacement, which is commonly conducted through acidification using strong acids, like sulfuric or hydrochloric acid.[12,13,15,16] Due to the nature of chemical reactions between liquids leading to a sparely soluble crystalline product like TA, the reaction induces high supersaturations. Thus, more TA is present in the liquid phase than possible in thermodynamic equilibrium. In order to restore equilibrium, TA instantly precipitates as fine crystals. These crystals complicate downstream processing and differ substantially from the industrial standard purified TA (PTA). In order to successfully recover and reuse terephthalic acid, its properties regarding its reapplication as one monomer for PET polycondensation must meet industrial specifications to close the loop using BMR.[17]

1.2 Scope and Approach

Despite the significant potential of the depolymerization pathway, the TA crystallization from DST solution is still not fully developed. To date, only a limited number of studies have been dedicated on investigating this step. Among these, Lee et al. follow a one-step approach by using an organic solvent mixture in batch precipitation leading to a final recycled TA (rTA) suitable for repolymerization.[18] Wu et al. precipitated rTA first and subsequently recrystallized the crude TA in an organic solvent by cooling crystallization.[19] However, the rTA of these studies does still not possess PTA properties. Moreover, the use of organic solvents instead of water for PTA purification increases downstream efforts.[17,20,21] Nevertheless, the separation of synthesis and final product purification and design is a sensible approach.[10,19]

Hence, this thesis focuses exclusively on the first step: the advantageous and straightforward recovery of TA through precipitation. The understanding of this first step is of critical relevancy to exploit this technique in its full potential.

Therefore, the present work aims for identification of process parameters to (e.g. temperature, precipitation acid type) which increase TA crystal size and improve filterability. Based on the demand for a process with a straightforward applicability in order to be industrially implemented, a standard stirred tank reactor setup is used throughout this work.

The investigation starts with screening in a model reactant system and progresses to depolymerized waste PET reactants containing impurities. Among PET impurities, particularly isophthalic acid (IA), a TA isomer, requires precise control over its integration into rTA crystals. Thus, alongside assessing decolourisation potential, process parameters are examined with regard to their efficiency in reducing IA content in rTA. Furthermore, with focus on operating costs, productivity and scale-up, a continuously operated precipitation step is developed, subsequently. Moreover, continuous operation can improve crystallization behaviour by reducing supersaturation and naturally providing crystal seeds.

Finally, a precipitation concept is proposed, emphasizing the benefits that can be achieved through TA precipitation, while recognizing the necessity for a subsequent recrystallization step.

In conclusion, this research work represents a significant advance for PET circularity, by providing practical and innovative approaches on improving TA purity, recovery and processability. Precipitated rTA could be used directly in polycondensation in mixtures with PTA. Regarding pure rTA application, this research can be a starting point for consecutive developments for rTA recrystallization. Alternatively, rTA can be used as feedstock for existing PTA purification plants, whose capacity utilisation will be reduced in circular PET economy.

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2 Crystallization Fundamentals

The following chapters introduce the fundamental relations of the determining factors and processes regarding crystallization. They aim to provide an overview about the driving force of crystallization and the effects leading to solid formation and subsequent growth. The information within is given on a descriptive level rather than calculative. A detailed insight including the mathematical aspects, model approaches and theories on crystallization fundamentals can be found in Mersmann, Mullin and Myerson.[22–24]

2.1 Supersaturation

Given a defined set of conditions (e.g. temperature, pressure), supersaturation describes the state of a solution containing a higher amount of solute than in thermodynamic equilibrium. The supersaturated solution regains its equilibrium state by formation of a solid phase. Therefore, supersaturation is the fundamental driving force and essentially necessary for crystallization. In strict terms, the supersaturation is a simplification aimed at addressing the difference in chemical potential μ between the solute component in solution and its crystalline state, which is responsible in the formation of a new solid phase, as expressed in Equations 2-1 and 2-2.

$$\Delta\mu = \mu_{solution} - \mu_{crystal} = RT \cdot ln\left(\frac{a_{solution}}{a^{*}_{crystal}}\right) \tag{2-1}$$

$$\frac{\Delta\mu}{RT} = ln\left(\frac{a_{i,solution}}{a^{*}_{i,crystal}}\right) = \ln\left(S_a\right) \tag{2-2}$$

An exact expression of supersaturation requires the knowledge of the effective concentrations a_i (activities), which are not always known in industrial applications. Therefore, a simplified practical approximation of the dimensionless supersaturation ratio S is given by Equation 2-3 in terms of molarity (c) and molality (m).[22]

$$S_c = \frac{c}{c^*} \; or \; S_m = \frac{m}{m^*} \qquad 2\text{-}3$$

It presumes activity coefficients to be 1 (ideal) and differs substantially from activity-based supersaturation ratios. Regarding the dependencies (e.g. temperature) of the solubility limit, supersaturation can be induced by several ways e.g. by cooling, solvent removal or drowning out. These procedures share the mutuality of a reasonable solubility of the target solute in the liquid phase. Instead, concerning reactive crystallization or precipitation, supersaturation is induced by a chemical reaction, e.g. $A_{(aq.)} + B_{(aq.)} \rightarrow C_{(s)}$. Thus, the sparingly soluble target solute C is produced as soluble reactants A and B are contacted. For description of the supersaturation ratio for these systems an expression in dependence of the concentration solubility product K_{SP} (saturated state) is appropriate and shown in Equation 2-4.

$$S_c = \frac{c_{AB}}{c_{AB}^*} = \frac{\left(c_A^{\nu_A} \cdot c_B^{\nu_B}\right)^{\frac{1}{\nu_A+\nu_B}}}{K_{SP}} \; with \; K_{SP} = \left(c_A^{\nu_A} \cdot c_B^{\nu_B}\right)^* \qquad 2\text{-}4$$

However, as for the supersaturation ratio based on molarities and molalities, the use of concentrations instead of activities is limited to low concentrations for realistic approximations. The necessary activity coefficients can be approximated by thermodynamic models e.g. extensions of the Debye-Hückel equation like the Bromley equation[25] or UNIFAC models in addition to empirical approaches by Meissner.[22,26] For details on these activity coefficient approaches and their calculations it may be referred to Zemaitis et al. as well as Luckas and Krissmann.[26,27]

Nevertheless, the given Equation 2-4 describes the fact that a low solubility leads to high supersaturation values. Additionally, the velocity of the chemical reaction leads to a fast build-up of the supersaturation that cannot be depleted by molecular growth.[28] Instead a high number of small nuclei is formed in order to reduce supersaturation.[29] This phenomenon to so called homogeneous nucleation (see 2.2) leads to reactive crystallizations being complex and difficult to control.[22,24]

2.2 Nucleation

The starting point for crystallization is the formation of solid nuclei representing the smallest arrangement of a number of molecules being able to exist. Prerequisite to this stochastic process is a system in non-equilibrated supersaturated condition which is the driving force for reduction of supersaturation by aggregation. This condition is described as metastable zone whose width depends on the respectively applying nucleation mechanisms.[23] The classification of the different nucleus formation mechanisms is displayed in Figure 2-1.

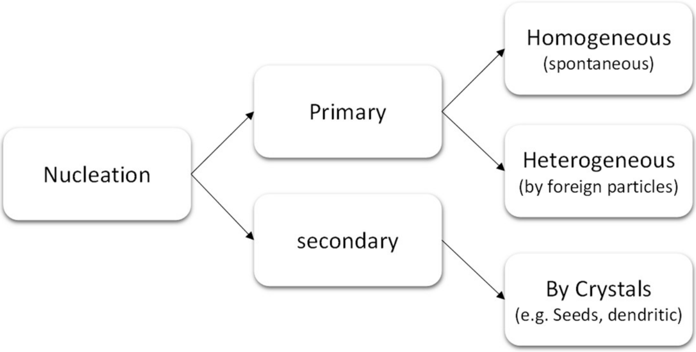

Figure 2-1 *Basic mechanisms of nucleation, adapted from Mullin and Myerson.*[22,23]

Spontaneous nucleation from particle free solution is referred to as homogeneous nucleation. If foreign matter (e.g. dust, foreign surfaces) is present in an otherwise crystal free solution, heterogeneous nucleation occurs. These two are grouped as primary nucleation mechanisms and require high supersaturations. Under the presence of crystals of the same kind suspended in solution, secondary nucleation comes into effect, requiring significantly lower supersaturations.

The origin of theories on homogeneous nucleation are early works on droplet nuclei forming from supersaturated gas,[30] which was extended in early works from Becker and Döring[31], and Turnbull and Fisher [32] to derive in the classical nucleation theory (CNT). Despite ongoing research, until today experimental verification of theoretical predicted nucleation rates has not been achieved, due to the complex interplay of influencing factors and measurement limitations.[33–35] In the following the fundamental understanding behind the CNT will be presented. For extensive calculative approaches on the estimation of nucleation rates it may be referred to the work of Mersmann and Mullin.[22,24] For an overview on non-classical nucleation theory it may be referred to Myerson.[23]

Starting point for this perspective is a metastable solution without foreign particles nor impurities. Prerequisite for a new phase to develop is the formation of an interface, requiring additional enthalpy in the system. This new interface appears as the result of single molecules spontaneously approximating and joining due to local density and concentration differences. Despite the reversibility of this event, at sufficiently high supersaturation the birth of these embryos surpasses their decay and eventually leads to the formation of larger units. The build-up of these clusters leads to an increase in interfacial tension γ_{CL} between crystal and surrounding liquid. In parallel, this cluster formation process releases free volume-enthalpy ΔG_V.

Figure 2-2 displays the free surface and volume enthalpies and their sum, the total enthalpy ΔG over the nucleus size, L, increase in free surface enthalpy ΔG_A.

As the positive free surface enthalpy is proportional to the square of the nucleus size whereas the negative free volume enthalpy is proportional to nucleus size cubed, their sum features a maximum value ΔG_{crit} at a critical size, L_{crit}. For a spherical particle this critical size can be calculated by Equation 2-5, with k_B as the Boltzmann constant and the temperature T. Nuclei being smaller than this critical size decompose while nuclei being larger can continue to grow.

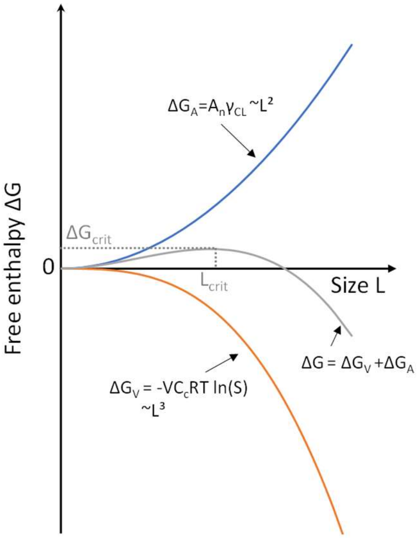

Figure 2-2 Free enthalpy over nucleus size L, adapted from Mersmann.[24]

$$L_{crit} = \frac{4 \cdot \gamma_{CL}}{k_B \cdot T \cdot \ln S} \qquad 2\text{-}5$$

In the following, a CNT approach on calculation of the homogeneous nucleation rate B_{hom} is presented, as displayed in Equation 2-6. It is based on three fundamental factors which are shortly introduced subsequently.

$$B_{hom} = n_{crit} \cdot k \cdot Z \qquad 2\text{-}6$$

The first factor is the number concentration of critical clusters n_{crit} which, assuming random collision of molecules can be described through a Boltzmann distribution, with n_0 being the number concentration of monomers in supersaturated solution (Equation 2-7).

$$n_{crit} = n_0 \cdot e^{-\frac{\Delta G_{crit}}{k_B \cdot T}} \qquad 2\text{-}7$$

The rate at which these clusters can cross the thermodynamically stable barrier is represented by the impact coefficient k which is displayed in equation 2-8, as derived by Mersmann and Kind.[24,36] It additionally depends on the surface area A_c of a cluster and the diffusion coefficient D_{AB}.

$$k = \frac{3}{4} n_0^{\frac{4}{3}} \cdot D_{AB} \cdot A_c \qquad 2\text{-}8$$

At last, the Zeldovich factor Z is introduced in Equation 2-9 to account for the probability that a cluster reaching the critical diameter continues to grow. It represents the imbalance between equilibrium and steady state distribution as the clusters constantly cross the critical barrier.[24] Within this equation, i_c displays the number of monomers contained in a critical cluster.

$$Z = \sqrt{\frac{\Delta \mathrm{G}_{\mathrm{crit}}}{3 \cdot \pi \cdot k_B \cdot T \cdot i_c^2}} \qquad 2\text{-}9$$

Generally, homogeneous nucleation is dominating at high supersaturations common for reactive crystallization and precipitation and displays a maximum rate. However, under industrial conditions it is accompanied by heterogeneous and secondary nucleation.[24]

Nucleation under presence of foreign surfaces is described as primary heterogeneous nucleation. Their presence can reduce the activation barrier of nucleation which depends on the contact angle Θ between the surface and the clusters prior to nucleation. [23,24] Therefore, with respect to the wetting behaviour three cases can be distinguished. If no wetting of liquid on the foreign surface occurs ($\Theta = 180\,°$), nucleation is not affected and can be regarded as homogeneous. A partial wetting ($180\,° > \Theta > 0\,°$) reduces the surface excess energy and thus a lower overall free excess energy is required for nucleation compared to homogeneous nucleation. For the theoretical case of complete wetting ($\Theta = 0\,°$), the activation barrier for nucleation is reduced to an extent as if parent crystals were present in supersaturated solution.[22,23,37]

However, nucleation under the presence of crystals of the same species differs from the previously introduced primary nucleation and is referred to as secondary nucleation. The underlying mechanism is explained by several theories mainly aiming to describe the connection between nuclei and parent crystal. While theories on the effect of fluid shear exist as well, in the following only mechanisms based on dendritic crystals and contact nucleation will be introduced closer. High supersaturations as present in precipitation processes lead to the formation of needle and dendritical structures. Due to their mechanical instability, parts of these structures can break and the resulting fragments provide new surface for nucleation. On the contrary, in contact nucleation the physical impact between the crystal and a stirrer, reactor wall or other crystals results in surface damage. This surface defect provides a site for nucleation in addition to the lose fragments broken off the crystal.[23]

With regard to industrial applications and conditions (e.g. presence of dust, bubbles, rough surfaces) pure homogeneous nucleation displays a rare phenomenon and heterogeneous nucleation is more common.[22] Additionally, formation of crystals during crystallisation leads to their direct presence in a reactor inducing secondary nucleation. It displays the dominating nucleation mechanism in continuous or seeded crystallization processes, as it requires substantially lower supersaturations compared to primary nucleation.[23]

2.3 Growth

Crystal growth is the second phase that follows after initial nucleation and is often described by the linear growth rate as the increase of particular crystal face over time. Due to its complexity, this process is still not fully understood today.[22–24] The single fundamental steps necessary for crystal growth can be summarized as follows. Considering a supersaturated bulk solution, the contained solvated ion or molecules must first diffuse through the diffusion-boundary- and adsorption layer. This is followed by a surface diffusion to the integration site. In case of a solvated species, desolvation follows in order for the unit to be integrated into the crystal lattice. Finally, the released solvent molecules diffuse through the diffusion-boundary- and adsorption layer back into the bulk media.[22] Depending on the respective crystallization process, growth can be either controlled by the diffusion or integration (reaction) process. This growth pathway and the respective driving forces are depicted in Figure 2-3, according to Mullin.[22]

For low supersaturations crystal growth is controlled by the integration of new ions or molecules into the crystal lattice. This integration is significantly influenced by the roughness of the crystal surface. Thus, a suitable energetically favourable site features a maximum number of adjacent faces for a growth unit to attach to. There are several theories trying to explain the origin of these kinks and steps like the BCF model (Burton-Cabrera-Frank). It assumes that defects inside

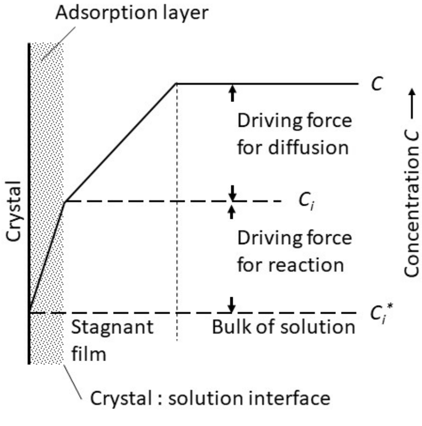

Figure 2-3 *Driving forces in solution crystallization with regard to concentration, adapted from Mullin.*[22]