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CZASOPISMO POŚWIĘCONE CHEMII, TECHNOLOGII i PRZETWÓRSTWU POLIMERÓW

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Solid-state polycondensation (SSP) as a method to obtain high molecular weight polymers

Part I. PARAMETERS INFLUENCING THE SSP PROCESS

Summary — The paper is a literature review concerning the solid-state polycondensation (SSP) method. SSP is a competitive method of polymer synthesis to conventional melt polycondensation. The molecular weight of polymers obtained according to this method is exceptionally high and the polymer properties are also improved. In most cases the starting materials for SSP are in the form of flakes or powder. The process involves heating of the starting materials at the temperature between the glass transition temperature (T_g) and melting temperature of partially crystalline prepolymer (T_m). The reaction leading to an increase of molecular weight occurs between the chains terminal groups in the amorphous phase of semicrystalline polymer. The reaction equilibrium is shifted in favor of the formation of polymer due to by-products removing from the reaction system by inert gas flow or under vacuum. Due to the use of lower temperature than that usually applied in melt polycondensation, side reactions and thermal degradation of the product are limited. In addition, the process does not require complicated equipment and is environmentally friendly because no organic solvents are used. However, when the polymer contains larger amounts of by-products or a small extent of crystalline phase, sticking of the polymer particles can take place. In this case, the reaction proceeds not in solid but in melt phase, the contribution of the reactions between the terminal functional groups and the reactive groups of the middle part of polymer chains is much higher, which leads to higher degree of dispersity, but not to an increase in the polymer molecular weight. This paper presents the fundamentals of the SSP process and its advantages in comparison with other polycondensation methods. The kind of polymers that can be obtained with this method is described. In addition, the factors influencing the process and the properties of final products are discussed.

Keywords: solid-state polycondensation, crystallinity, polyamides, polyesters, polycarbonates, poly(lactic acid).

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POLIKONDENSACJA W STANIE STAŁYM — METODA OTRZYMYWANIA POLIMERÓW O DUŻYM CIĘŻARZE CZĄSTECZKOWYM. Cz. I. PARAMETRY WPŁYWAJĄCE NA PRZEBIEG PROCESU

Streszczenie — Artykuł stanowi przegląd literatury dotyczący polikondensacji w stanie stałym (SSP). SSP jest konkurencyjną metodą syntezy w stosunku do tradycyjnej polikondensacji w stopie. Za jej pomocą można otrzymywać polimery o dużym ciężarze cząsteczkowym, a co za tym idzie, o konkurencyjnych właściwościach. Synteza polega na ogrzewaniu wcześniej otrzymanego, rozdrobnionego i poddanego procesowi krystalizacji, prepolimeru w temperaturze pomiędzy temperaturą zeszklenia (T_g) a temperaturą topnienia częściowo krystalicznego polimeru (T_m). Proces odbywa się w atmosferze przepływającego gazu obojętnego, bądź pod obniżonym ciśnieniem. Zastosowanie obniżonej temperatury, w stosunku do stosowanej w metodzie polikondensacji w stopie, ogranicza udział zarówno reakcji ubocznych, jak i termicznej degradacji produktu. Poza tym proces ten nie wymaga skomplikowanej aparatury, a ze względu na niestosowanie rozpuszczalników organicznych jest przyjazny dla środowiska. Jednakże podczas prowadzenia procesu (na skutek obecności wilgoci, małocząsteczkowych produktów ubocznych lub małego udziału fazy krystalicznej) może dochodzić do sklejania się cząstek polimeru. Wtedy reakcja przebiega już nie w stanie stałym, lecz w stopie i zwiększa się udział reakcji z udziałem wiązań ze środkowych części łańcuchów, co nie prowadzi do wzrostu ciężaru cząsteczkowego, a jedynie do redystrybucji długości łańcuchów. W niniejszej pracy przedstawiono podstawy procesu SSP i jego zalety w porównaniu z innymi metodami prowadzenia polikondensacji. Opisano, jakiego typu polimery można otrzymywać tą metodą. Poza tym wyjaśniono, jakie czynniki mają wpływ na przebieg procesu, ciężar cząsteczkowy i właściwości produktów końcowych.

Słowa kluczowe: polikondensacja w stanie stałym, krystaliczność, poliamidy, poliestry, poliwęglany, poli(kwas mlekowy).

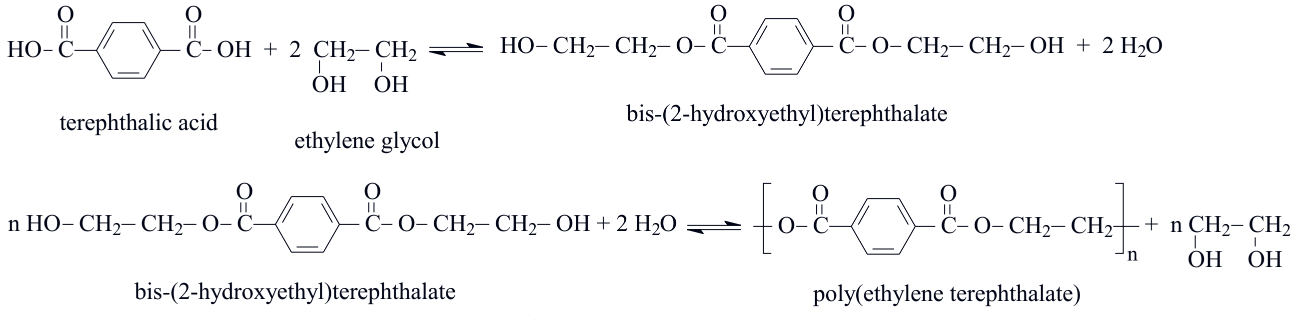
INTRODUCTION

History of polycondensation in the solid state (SSP) has its beginning in 1939 when Flory received with this method high molecular weight polyamide 66 [1]. However, the SSP technology has become a popular synthetic method of semi-crystalline polymers such as polyesters, polycarbonates as well as polyamides relatively late. These polymers are generally prepared in a stepwise reaction between difunctional monomers, which is accompanied by the formation of a low molecular weight by-product [2]. Solid monomers can be used directly in SSP as well as solid prepolymers (polymers obtained by melt polycondensation). The former process is referred to as direct SSP and the latter one as post-SSP (SSP finishing) [3, 4]. According to the post-SSP method, after polycondensation in the melt phase, the molecular weight of the resultant polymer is further increased in the solid-state polycondensation. The reaction schemes for the formation of typical polymers obtained currently *via* the SSP method are presented in Schemes A—E.

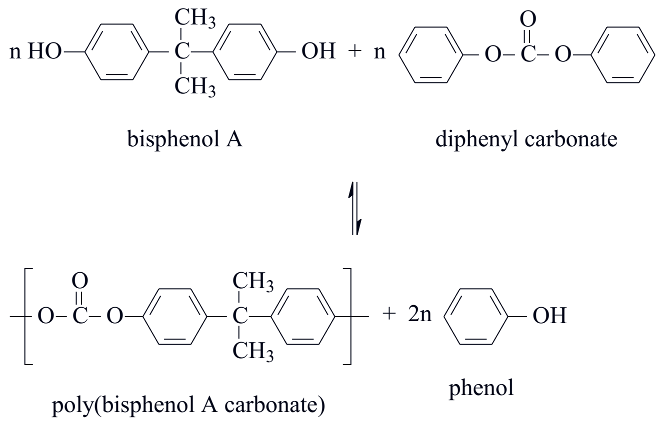
It should be emphasized that industrial application of SSP refers primarily to the production of polyamides and polyesters. SSP is used mainly for production of poly(ethylene terephthalate) (PET) [2, 5—8]. It should be added that SSP is also an efficient recycling technique [9, 10], through which the molecular weight of the postconsumer polymer such as PET is increased, and the resulting material can be processed without mechanical properties deterioration.

Molecular weights of other polyesters such as poly(butylene terephthalate) (PBT) [11], poly(trimethylene terephthalate) (PTT) [12] and poly(ethylene naphthalate) (PEN) [13—15] can also be increased with the SSP method.

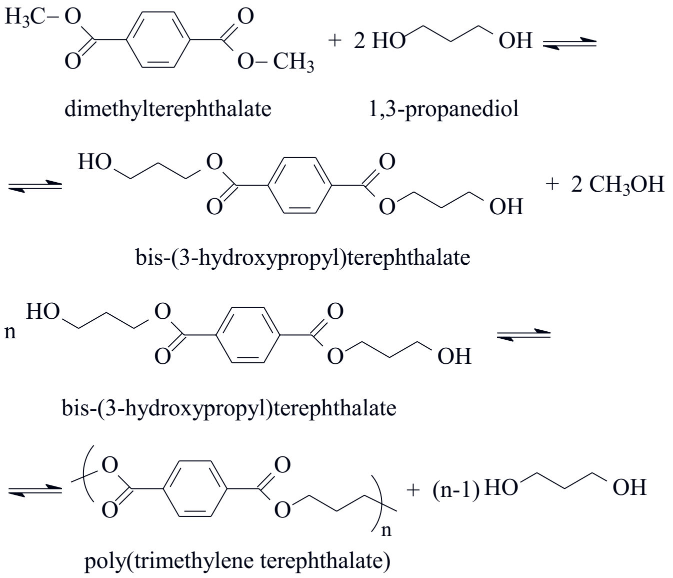
Novel direct polycondensation of 4-hydroxybenzoic acid by means of reaction-induced crystallization of oli-



Scheme A. Synthesis of poly(ethylene terephthalate) (PET)



Scheme B. Synthesis of poly(bisphenol A carbonate) (BPA-PC)

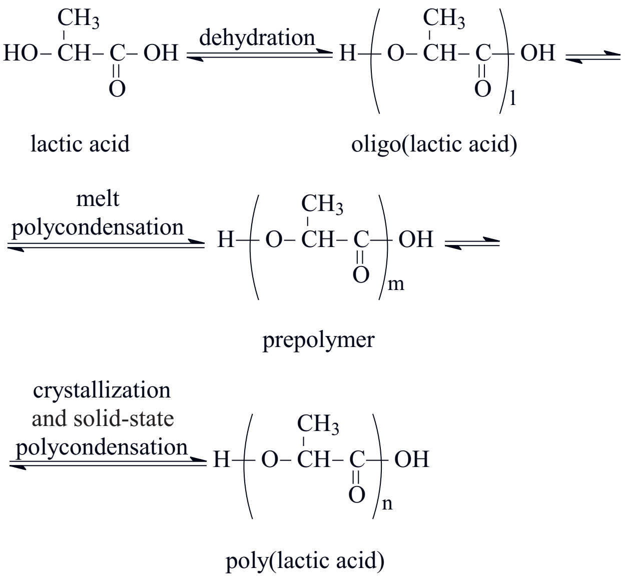


Scheme C. Synthesis of poly(trimethylene terephthalate) (PTT)

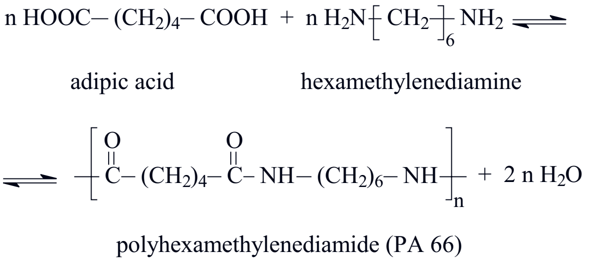
gomers under nonstoichiometric conditions was recently reported by Kimura and coworkers [16]. This process is presented in Scheme F.

The authors have found that high molecular weight poly(*p*-oxybenzoyl) could be prepared from 4-alkyloxybenzoic anhydride and 4-hydroxybenzoic acid in a reaction carried out in liquid paraffin. The polycondensation proceeds under nonstoichiometric conditions according to the following mechanisms: when the molecular weight of oligomers exceeds a critical value, they start to crystallize. End-free oligomers are preferentially crystallized due to the lower solubility. Though end-capped oligomers are also crystallized, polycondensation proceeds with eliminating end-capping groups by transesterification just when they are crystallized.

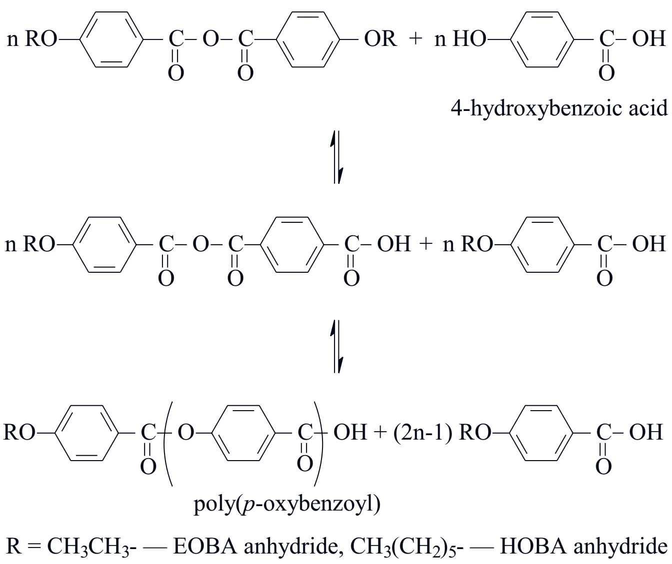
Alternatively to the phosgene method, bisphenol A polycarbonate is currently produced from diphenyl carbonate with the SSP method [17—20]. It is worth mentioning that diphenyl carbonate is obtained by green chemistry method from CO through dimethyl carbonate and phenol [21].



Scheme D. Synthesis of poly(lactic acid) (PLA)



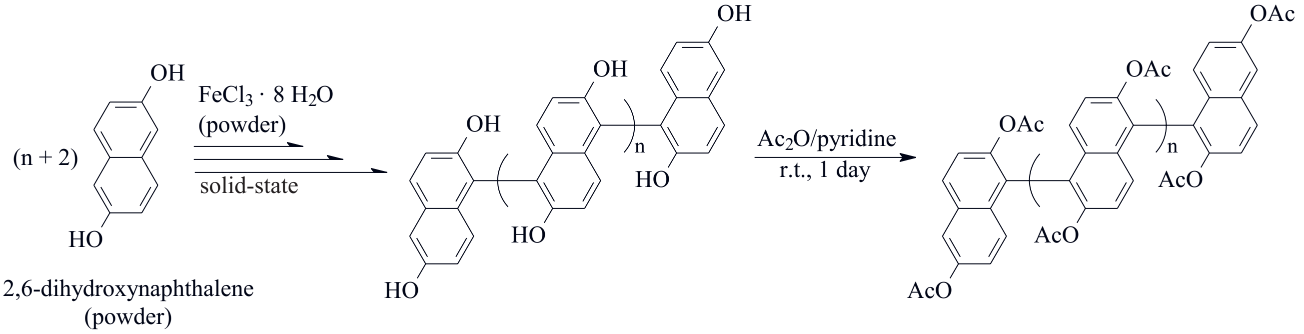
Scheme E. Synthesis of polyhexamethylenediamide (PA 66)



Scheme F. Direct polycondensation of 4-hydroxybenzoic acid

Industrial application of SSP is also widely used for polyamide 6 and 66 production [2, 7, 22—24].

Besides of esterification, transesterification and amidation also other types of reactions leading to high molecular weight polymers can be utilized in the solid-state processes. Recently, Suzuki and Yatsugi presented



Scheme G. Solid-state oxidative polycondensation of 2,6-dihydroxynaphthalene

a novel type of oxidative-coupling SSP. They carried out 1,5-oxidative-coupling of 2,6-dihydroxynaphthalene, as it is shown in Scheme G, after grinding crystals of 2,6-dihydroxynaphthalene-benzylamine complex with FeCl$_3$ · 6 H$_2$O powder in a mortar. The resultant atactic poly(2,6-dihydroxy-1,5-naphthylene) of *ca.* 10 000 molecular weight was obtained at room temperature after 24 h [25].

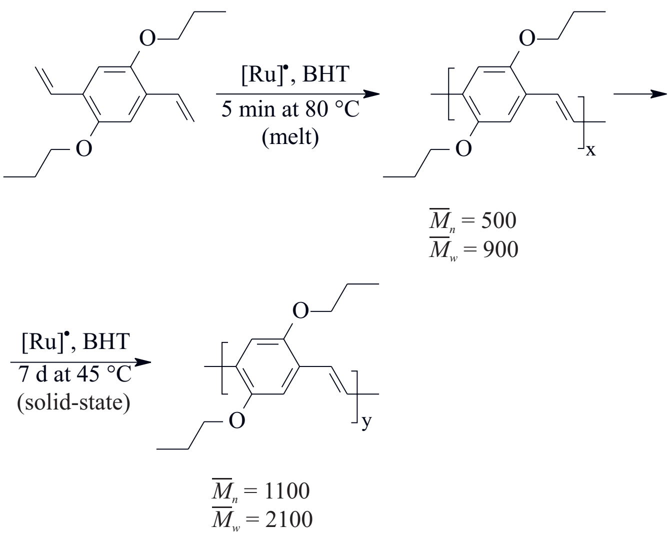
It was also found that the adenine-derived supramolecular telechelic polymer self-assembled in the solid-state to yield polymers with film- and fiber-forming capabilities. Rowan *et al.* [26] reported the synthesis of nucleobaseterminated (N^6-anisoyl-adenine and thymine) low-molecular weight poly(tetrahydrofuran) macromonomers (number-average molecular weight $\overline{M}_n$ = 2000) and supramolecular step growth polycondensation of these 2,6-dihydroxynaphthalene macromonomers through the utilization of the noncovalent bonds.

Solid-state procedure was applied for olefin metathesis of rigid-rod acyclic diene metathesis (ADMET) and ring-closing metathesis (RCM). Oakley and Wagener [27] took attempts to polycondense 1,4-dipropoxy-2,5-divinylbenzene in a bulk ADMET to afford dialkoxy poly(phenylene vinylene). The reaction, which is presented in Scheme H, was continued in the solid-state, effectively doubling the molecular weight. Solid-state RCM was investigated with a variety of solid dienes and metathesis catalysts such as second generation Grubbs ruthenium catalyst. However, rather low conversion of monomers was observed.

As it was earlier mentioned, the SSP process enables formation of polymers with high molecular weight, which cannot be achieved in the typical melt phase process. The additional advantages of the solid state method compared to the melt phase one are as follows:

— difficulties associated with the stirring of the viscous melt and heat transport are reduced or eliminated;

— thermal degradation and side reactions are limited due to lower reaction temperatures used (the PET obtained according to the SSP method can be used for production of bottles with acceptable concentration levels of acetaldehyde — a by-product of degradation, which even small concentration can affect the taste of carbonated soft drinks and mineral water);



Scheme H. Melt polycondensation followed by continued polycondensation in the solid-state of 1,4-dipropoxy-2,5-divinylbenzene with second generation Grubbs ruthenium catalyst for 7d

— lower investment and running costs of the SSP process, which does not require vital for the melt phase ultimate high temperature and vacuum (in the case of PET the investment costs are much lower and the running costs are approximately half of these for the process carried out in the melt phase).

The polycondensation process proceeding in the solid-state is complex and still not fully understood. The reason is the influence of the physical processes of diffusion and crystallization on the reaction kinetics. The SSP process proceeds when particles of semi-crystalline polymer are heated to the temperature higher than the glass transition temperature (T_g) of the amorphous phase but lower than the melting temperature (T_m) of the crystalline phase. To shift the reaction forward, not only the end-groups of the polymer chains should contact each other, due to conformational movements, but also any reaction by-products, such as water or other small molecules must be removed from the solid phase. Moreover, a solid polymer matrix undergoes transformation through crystallization processes, which leads to confined end-groups and decreasing by-product molecules mobility.

It is generally accepted that the chemistry of SSP process is the same as in the melt and chemical reactions proceed in the amorphous phase. This implies that the polymer chain end-groups, catalyst and by-product are present only in the amorphous phase [7, 28]. Besides reactions leading to a polymer of high molecular weight, thermal degradation accelerated by catalyst can also take place [6, 29]. However, it should be noticed that it occurs principally at higher temperatures in the melt phase, while in the solid-state it is less significant.

As is presented in Schemes A—E, esterification, transesterification and amidation are the main reactions responsible for molecular weight increase in these polymers. These reactions are considered to be reversible and of second-order [30]. As it was earlier mentioned, to drive the reaction forward in the direction of the high molecular weight polymer the reaction by-product must be continuously removed from the reaction medium. Thus, this process is affected by the following parameters:

— the rate of the reversible chemical reaction,

— the diffusion rate of the reaction by-products through the polymer matrix to the particles surface,

— the diffusion rate of the reaction by-products from the particle surface to the gas.

The whole process rate is governed by the slowest step.

Process controlled by the chemical reaction rate

When the diffusion rate of by-products is much faster than the rate of chemical reaction, then the concentration of the by-products is very low throughout the particle and the rate of the reverse reaction can be neglected [30]. The process is characterized by a linear increase of the product molecular weight with respect to time and is also dependent on the starting molecular weight and the reaction rate constant.

Process controlled by the diffusion rate

If the diffusion rate of the by-product through the solid amorphous phase is much slower than the chemical reaction, then the reaction can be considered to be at equilibrium throughout the polymer particle [31]. The process rate is dependent upon the particle size, diffusion rate of the by-product, starting molecular weight of the polymer, and the reaction equilibrium constant. In addition, the particles can be expected to have a radial viscosity profile due to a by-product concentration profile through the polymer particle with the molecular weight of product increasing as the by-product concentrations decreases in the direction of the particle surface [11, 32].

Process controlled by the surface diffusion rate

When inert gas flow velocity is high, the particle surface by-product concentration is maintained at an equilibrium value determined by the by-product concentration in the gas. Under these conditions, the mass transfer from the surface is balanced by the diffusion within the particle to the surface. However, if the gas flow is reduced the gas-side mass transfer coefficient will also decrease until eventually the mass transfer from the surface is slower than the diffusion to the surface. At this point, the surface by-product concentration increases and the overall diffusion rate of the by-products is reduced. This leads to a decrease in the rate of the reaction and the process is controlled by the surface diffusion rate. The reduction in reaction rate due to surface diffusion has been shown to occur at gas flow velocity below 1.5 m^3/min [33].

PARAMETERS INFLUENCING SSP

Each above presented step is influenced by the reaction conditions. Among these parameters are both physical and chemical factors such as reaction temperature, prepolymer molecular weight (initial group concentration), size and geometry of particles, vacuum, gas flow, crystalline phase content and the kind of catalyst system. The main factors and their influence on SSP process are discussed below.

Reaction temperature

According to many authors [7, 34] the reaction temperature is the most important factor influencing the SSP process. It may interfere with the chemical reaction, the mobility of the functional end-groups, and the by-product diffusion [35]. As a rule, the reaction should be carried out above T_g and below T_m of the crystalline phase of the polymer. However, sufficient mobility of the end-groups is required to ensure reaction at an acceptable rate [36]. It has been shown that the synthesis of PET does not begin until 150 °C is reached, although the rate does not become industrially significant until the temperature is above about 200 °C [37]. Taking the above into account, SSP cannot be applied for polymers characterized by significantly low T_m value. The temperature range in which SSP can occur is rather narrow because on the one hand, the temperature should be as high as possible to maximize the reaction rate, but on the other hand it has to be sufficiently below T_m to prevent the polymer particles from sticking.

The SSP activation energy (E_a) indicates the dependence of the reaction temperature on the SSP rate constant. For polyamides the values of E_a are reported to be between 10.5 and 81.5 kcal/mol, and in the case of polyesters — between 15.0 and 42.5 kcal/mol. In comparison to E_a for melt processes the mentioned values are insignificantly higher [36, 38].

It is noted that the temperature range in the SSP process can be wider when the melting point of the crystalline phase is high. Then the influence of the reaction temperature on the SSP rate is restricted by T_g and T_m [39].

Due to the increase of the reaction temperature, the concentration of inactive end-groups decreases because some of them are moved into the amorphous phase as a consequence of the polymer crystallization at a higher temperature. To summarize, the optimal temperature for SSP should be 10—40 °C below T_m of the prepolymer to eliminate particle agglomeration.

Reaction time

When the process is controlled by the chemical reaction rate, then the increase in molecular weight is almost linear with time. This was shown for PET synthesis at 160 °C with a particle size of *ca*. 2.1 mm [40]. However, when the standard particle diameter is higher and temperature is above 200 °C, the reaction rate decays over time. Typically, the molecular weight increase is proportional to the square root of time [37, 41, 42]. Such behavior is typical for a process governed by both chemical reaction and diffusion within the material [40]. It should be noted that as a rule the reaction time of the process carried out according to SSP method is longer than that requiredin the molten state.

Prepolymer initial molecular weight

The final product is characterized by higher molecular weight when the concentration of end-groups in the initial polymer is lower. It corresponds to the high value of initial molecular weight. According to the two-phase model, the high value of initial molecular weight guarantees a more effective confinement of the amorphous phase and, therefore, high concentration of the reactive chain ends in the reaction area [43]. In another paper it is pointed out that in the case of a lower molecular weight of prepolymer, it is easier for polymer chains to fit into crystal lattices, and as a result, a greater number of end-groups will be trapped and become inactive [44]. Schiavone [45] investigated the SSP process, starting from very low molecular weight poly(ethylene terephthalate) precursors and found that the overall rate of SSP for the low molecular weight precursors is significantly less than of conventional SSP. This reduction in rate was explained by differences in crystallinity.

The effect of prepolymer molecular weight on the SSP of diphenyl carbonate with bisphenol A using nitrogen as a sweep fluid was investigated by Kim *et al*. [18]. Prepolymers with different number average-molecular weights ($\overline{M}_n$ = 3800 and 2400) were synthesized using melt transesterification. At 120—190 °C, SSP of the higher molecular weight prepolymer ($\overline{M}_n$ = 3800) always resulted in higher molecular weight polymers, compared to the polymers synthesized using the lower molecular weight prepolymer ($\overline{M}_n$ = 2400). Both the crystallinity and the lamellar thickness of the polymers synthesized from the lower molecular weight prepolymer were significantly higher than for those synthesized from the higher molecular weight prepolymer. Higher crystallinity and lamellar thickness may lower the reaction rate by reducing chain-end mobility, effectively reducing the rate constant for the reaction of end-groups [18].

The effect of remelting on the SSP rate is associated with the end-group mobility. It has been found that the procedure of remelting, proceeding some times after starting SSP, leads to an increase in the polycondensation rate. This effect is a result of the homogenization of the reacting mass which facilitates the reaction between chain ends achieved through shortening the distance between end-groups [46, 47].

Additionally, the initial ratio of different end-groups' concentrations also plays an important role. For example in the case of PET, it has been indicated by many authors that SSP needs a specific ratio of initial carboxyl to hydroxyl end-group concentrations. It is because the main reactions of esterification and transesterification are competitive and the by-products formed (water and ethylene glycol, respectively) exhibit different diffusion rates in the solid phase. Moreover, the shape of reacting particles is also important and influences the ratio [COOH]/[OH]. A high hydroxyl ends concentration is optimal if PET is in the form of powder. Then the diffusion of the ethylene glycol becomes easier. In the case of larger particles to favor esterification a high concentration of carboxyl ends facilitating the diffusion of water is preferred [11, 48, 49].

Particle size

The particle size and size distribution play a crucial role during the SSP process with respect to its efficiency [14, 18, 33, 45, 50—53]. The starting materials for post-SSP may take on various physical shapes or geometry (*e.g.* pellets, flakes, powder or even fibers and thin films) [54]. The particle size distribution governs the molecular weight distribution, which itself determines the uniformity of quality. The particle size reduction is not only a quality but also an economic reason. The commonly used cubic chips size (2—4 mm) is reduced to that of the known small nylon chips (about 1.5 mm in diameter, spherical shape). Due to their irregular shape, however, determination of their average volume is difficult. Therefore, the definition of mass (in g) of 100 pieces has become popular.

In the case of direct SSP, the size of the prepolymer particles and its affecting SSP rate is not significant for grain sizes below 20—25 mesh [55]. Meanwhile, in the case of post-SSP, in particular, particle size strongly influences the overall rate when the diffusion of the by-product within the polymer particle is the decisive parameter, but this influence gets weaker when the process is controlled by both diffusion and reaction rates (Fig. 1) [11, 55, 56]. It is commonly accepted that a smaller size of prepolymer particles can lead to an increased SSP rate and consequently to a decrease of the residence time, due to the shorter diffusion distance and the larger particle surface area per unit volume.

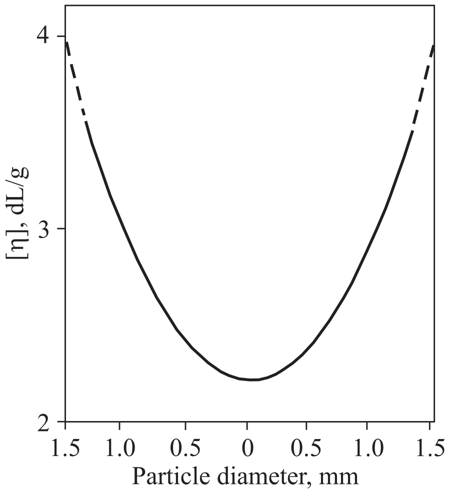


Fig. 1. Intrinsic viscosity [η] gradient within one poly(butylenes terephthalate) particle (according to [11])

It is a rule that the higher are polycondensation rates the smaller the particle size, due to the shorter diffusion path [57, 58], but conversion of molten polymer to chips is much easier than to fine particles. In addition, it is necessary to crystallize the solidified polymer before heating it at polycondensation temperatures in order to avoid coalescence of the particles, although further crystallization during the polycondensation process permits use of temperatures above the normal melting point of polymer [59, 60].

The effect of particle size on SSP rate is more substantial in the case of polyester prepolymers (for PET: a decrease in the particle diameter from 0.266 to 0.14 cm results in reducing the residence time by 56 %) [52], while in polyamides the reaction rate does not increase so dramatically with decreasing particle size (relative decrease of the particle diameter causes shortening residence time equal to only 3 %) [53].

Catalysts

Additives which can improve the SSP process can be divided into three types:

— typical catalysts such as metals or metal derivatives, acids, bases;

— reactive additives which can extend or branch molecular chains;

— inert additives which influence the process, but do not participate in the chemical reaction.

The additive or catalyst can be added to monomers, prepolymers, or polymers at different stages of the manufacturing process. The use of catalysts in the synthesis of typical SSP, preferably polymers such as polyesters and polyamides, accelerates both solid and melt phase reactions. In the solid state process any type of known catalysts, which causes polycondensation in the molten state, is also effective. In the case of direct SSP the catalysts are used to overcome the slow reaction rate and particles agglomeration. In the case of SSP of aminoacids the most efficient catalysts were among others [39]:

H_3BO_3 (1 %), MgO (0.2 %) > $(COONH_4)_2$ (0.5 %) > $(CH_3COO)_2Zn$ (0.5 %) > Na_2CO_3 (0.2 %) > CH_3COOH (0.6 %) > $(NH_4)_2SO_4$ (0.5 %) > $SnCl_2$ (1 %).

For polyamide 66 obtained by SSP method Khripkov *et al.* [61] reported catalysts effectiveness as H_3BO_3 > $(COOH)_2$ > H_3PO_4 > MgO. Meanwhile, Na_2CO_3, $NaHSO_4$, and $(SiO_2)_n$ were inactive. After a short period of SSP reaction time the linear oligomers are observed in the reactive mass [62]. In polyamide SSP, examples of catalysts used are mainly phosphorus compounds such as 2-(2′-pyridyl)ethyl phosphonic acid (PEPA) and sodium and manganous hypophosphite [3, 63]. More recently, hydroxyphenylmethyl phosphonate esters were found to catalyze the post-polyamidation in the solid phase through increasing the solution relative viscosity of the product by more than 50 % compared to the uncatalyzed process. This catalytic efficiency was correlated with the structure of the phosphonates. The authors proposed a mechanism, in which the additive mobility within the solid polymer implies the possibility of partial incorporation of the catalyst molecule into the polyamide structure as an end-group [64].

Finally, SSP catalysis constitutes a significant research area to overcome the main industrial SSP drawback, *i.e.*, low rate compared to the melt technique; in polyamides, the SSP rate increases by use of mainly phosphorus-based catalysts, which also were found to overcome sintering problems [64—66]. In the case of post-SSP, acidic compounds are mainly used as catalysts (*e.g.*, H_3PO_4, H_3BO_3, H_2SO_4). Because they are easily diffusing compounds, their presence accelerates the reaction rate. Meanwhile, in their absence the reaction rate is limited by diffusion of the autocatalyzing acid chain end-groups [67]. It was also proposed to use the thermoplastic polyurethanes as catalysts [68] as well as the sterically hindered hydroxylphenylalkylphosphonic ester [69].

It is known that transesterification does not proceed without the presence of a catalyst [70]. Antimony oxide (Sb_2O_3) is still the most widely used catalyst in the synthesis of PET and therefore it is also applied in SSP processes [71]. Sb_2O_3 catalyst offers a high catalytic activity and chemical stability, does not form color, and does not catalyze side reactions. Kokkolas *et al.* [71] showed that in the solid state the transesterification rate constant increases linearly with antimony trioxide (Sb_2O_3) concentration up to the level of 1000 ppm. The effect of Sb_2O_3, which is used as the main catalyst in production of PET by melt polycondensation, was studied on the SSP process. $\overline{M}_n$ of a PET prepolymer with an Sb_2O_3 content of 2000 ppm was increased from 18 350 to 40 800 after heating at 210 °C for 8 h under vacuum (2—3 Pa).

For very high molecular weight polyesters, titanium based catalysts such as sodium titanium butylate were applied [72]. It should be mentioned that other catalysts such as zinc acetate/Sb_2O_3 or cobalt acetate allow the synthesis of high molecular weight polyesters as well [73]. The molecular weight of PET was as high as 65 000 (zinc acetate/Sb_2O_3) or 120 000 when cobalt acetate was used as a catalyst.

Some authors claim the use of mixed metal based catalysts or combinations of traditional catalysts with additives. For example, combinations of antimony oxide (or germanium oxide, tetrabutoxy titanium) with heterogeneous co-catalysts such as hydrotalcites and stabilizers {*e.g.*, P-EPQ, tetrakis(2,4-di-*tert*-butylphenyl)[1,1-biphenyl]-4,4-diylbisphosphonite} [74] have been investigated. These combinations result in a two-fold increase of the intrinsic viscosity after SSP versus control sample, without increasing the metal content in the polymer or negatively influencing the processing properties. Antimony/tin combinations [Sb_2O_3/monobutyltin tris(2-ethylhexoate)] resulted in higher melt polycondensation and a small increase in the SSP rate, but also in a reduced acetaldehyde formation in subsequent processing steps [75].

The combination of titanium with magnesium based catalysts leads to 25 % time saving when SSP process is carried out at 190 °C with a selected molar ratio of titanium tetrabutoxide : magnesium acetate (1:1) [76].

Parthasarathy in [77] indicated that zinc-*p*-toluenesulfonate can be used as a more environmentally friendly catalyst for PET production. The molecular weights of the polymers obtained in the presence of zinc catalyst were decisively higher than those when using Sb_2O_3 or GeO_2. Furthermore, it is claimed that side reactions producing diethylene glycol units and color formation are minimized. Recently, Burch in [78] claimed that benzenesulfonic acid, as a completely metal-free system, can act as an SSP catalyst.

An additional attractive class of SSP accelerators are hydroxyphenylalkylphosphonic esters (Irganox 1425), which were originally developed for the SSP of polyester recyclates but are also found to be active in synthesis of virgin polyesters [79].

Recent publications on PET SSP indicate the catalytic effect of nanomaterials such as montmorillonite [80] as a result of increasing the nucleation sites for polycondensation. Other nanomaterials such as silica as catalysts for SSP process are also used [81]. Bikiaris *et al.* [82] used activated carbon black nanoparticles in SSP process of PET. At 230—240 °C an accelerating effect was found and higher intrinsic viscosities were measured, compared to neat PET.

Boussia *et al.* [83] studied the SSP process of obtaining polyamide 66 in the presence of clay nanocomposite. The authors suggested the positive effect of clay is of a synergistic origin attributed to nucleated crystal morphology that increased the concentration of reactive end-groups in the amorphous regions, to chain extension performed by clay SiOH groups, and to thermal protection of the polyamide matrix due to the presence of the nanoparticles.

The most popular catalytic system for lactic acid polycondensation carried out in the solid state is based on $SnCl_2$ and *p*-toluene sulfonic acid [84]. Essawy *et al.* [85] tested other catalytic systems such as Sb_2O_3/$SnCl_2$.

The influence of additives: poly(ethylene glycol) (PEG) and end-capped poly(ethylene glycol) [poly(ethylene glycol) dimethyl ether (PEGDME)] of $\overline{M}_n$ = 1000 on the synthesis of PET by SSP was studied by Gowd and Ramesh [86]. They have found that the plasticizers do not affect the crystalline morphology even though they influence the crystallization rate. PEG-incorporated samples form copolymers and they show improved SSP rates compared to SSP of PET oligomer under similar conditions. On the other hand, PEGDME samples cannot form a copolymer, and they retarded the SSP. Structure and morphology studies indicate that the PEG segments remain in the amorphous phase of the copolymer.

Crystallinity

Crystallinity affects the diffusion rate and the mobility of the end-groups, which are concentrated in the amorphous regions. It should be pointed out that the size, shapes and the packing of the crystals are important parameters influencing the mobility of the chain end-groups. According to the two-phase model [87], the reactive end-groups are located in the amorphous regions. As a result of the increase in crystallinity, both the concentration of end-groups in amorphous phase and the reaction rate are increased [40, 41]. Then, the process is controlled by chemical reactions. In contrast, as the reaction progresses, the mobility of the polymer chains decreases because the crystallinity increase and the removal of by-products from the reacting mass is hindered. In addition, as a consequence of a high degree of crystallinity, large fractions of long chains are immobilized and the attack of low molecular weight condensation by-products is impossible. Thus, reactions between end-groups are prevailing [19]. Then, the reaction is controlled by diffusion of the by-products. To sum up, the optimum degree of crystallinity should be about 40 % [40]. This value is high enough to prohibit particle agglomeration [88]. Additionally, the method by which the crystallization extends is also important and may affect the SSP process. Crystallization may be induced both by solvent evaporation and by crystallization from the melt [89]. The first technique is more preferable in cases of by-product diffusion controlled processes, in which the reacting particle size plays an important role because it can give a specific crystal size distribution, crystal perfection and structures of the prepolymer. But it has an important disadvantage: the solvents which are used to induce crystallinity, *e.g.* acetone, are inconvenient in large scale commercial plants, and they are difficult to remove. Organic solvents could be replaced by a supercritical medium, like supercritical CO_2 ($scCO_2$), as a factor inducing crystallization in the prepolymer [17]. In the case when the purity of the SSP product is required, the use of $scCO_2$ is beneficial, because the crystallization proceeds without pollution of the final product by solvent.

Kawai *et al.* [90] investigated the effect of the crystallization temperature on the crystal structure and its melting behavior of poly(L-lactic acid). PLLA was found to crystallize in the α form when the crystallization temperature (T_c) was higher than 120 °C, while significant change in lattice parameters was seen for T_c below 120 °C. The ratio of the α- and β-axis lengths begins to decrease with T_c below 120 °C and is $3^{1/2}$ below 90 °C, which suggests a new crystalline form with hexagonal packing, namely, the α' form. The possible reason for α' formation is discussed. High temperature WAXS and SAXS measurements showed that α' crystal transforms into ordered α form during heating. The transition takes place at 150 °C without any decrease in scattering intensity and without heating rate dependence.

Vacuum and gas transport

As it was explained earlier, efficient removal of the reaction by-products is extremely important in the SSP process. The presence of higher amount of the by-products in the reaction system may lead to degradation of the polymer. Thus, after long reaction time the molecular weight achieves a maximum and then starts decreasing. Moreover, fast removal of the volatile reaction products plays the most important role in shifting the equilibrium towards the formation of the high molecular weight polymer.

SSP can be carried out as well in vacuum or supported by the flow of an inert gas, usually nitrogen. The use of an inert gas or vacuum in SSP system serves three principal purposes: to remove the by-products, to inhibit polymer oxidation by excluding oxygen from the reactor atmosphere, and to heat the reacting mass (only from gas flow). Generally, there is no difference between the vacuum and gas flow methods. However, in the case of the vacuum method, fast removal of the by-products is affected by the applied pressure whereas in the gas flow method it depends on the flow rate of the inert gas employed. In SSP processes as the inert gases are predominantly used: nitrogen (N_2), carbon dioxide (CO_2), helium (He), superheated steam and $scCO_2$ [6]. In many cases, the characteristics of the inert gas to be employed must be taken into consideration, since it may influence the SSP process. For example, the differences in activities of employed gases are observed ($He > CO_2 > N_2$) [91]. Helium has a relatively higher diffusivity than either N_2 or CO_2, because of its smaller molecular size. Therefore, the application of He leads to an increase in the free volume growth rate and degree of polycondensation. Meanwhile, CO_2 is characterized by better solubility in the polymer than N_2 which can induce a plasticization effect, and improve the local mobility. The SSP process may involve heating under continuous inert gas flow (open system), where the by-product removal is dominant [6, 11, 59], or under a stagnant inert gas atmosphere (closed system), where the loss of monomers and oligomers is restricted [40]. The first one is preferable in the case of post-SSP, meanwhile the second one was used earlier in direct SSP. Practically, a combination of these two systems may be used. At first, heating in an inert atmosphere and then a flow of an inert gas take place [29]. This combination allows maintenance of the monomers and satisfactory removal of the by-product in order to favor the polycondensation reaction.

SOLID-STATE POLYCONDENSATION IN DISPERSED MEDIUM

Carrying out polycondensation in a dispersion of small particles of oligomers does not cause an increase in viscosity with molecular weight increase and the condensation reaction by-products can be easily removed, which favors a faster conversion to high molecular weight polymers than in conventional melt or solution processes, where diffusion to the surface is a rate controlling factor. According to this procedure Pasquet and Spitz [50] carried out the polycondensation of 11-aminoundecanoic acid.

Decalin (decahydronaphthalene), which is an inert saturated cyclic hydrocarbon and reacts with neither the monomer, nor with the condensation by-product (*e.g.* water), was used as a dispersed medium. A liquid-liquid suspension step was used at the beginning of the reaction in order to melt, disperse and break the crystallinity of the monomer, then the liquid droplets were solidified by cooling. During the polycondensation, the temperature was raised in successive steps in order to maintain the particles in the solid state. With a convenient treatment, it was possible to obtain a polymer powder with a defined particle size distribution and to reach fairly high molecular weights. This study was carried out with 11-aminoundecanoic acid, an AB type monomer which eliminates the problems of stoichiometry and for that reason, appears as a simple case.

Recently Gantillon *et al.* [92] proposed a new process for the SSP of PET. It is shown that by correctly choosing the pre-polycondensation conditions it is possible to crystallize the product and to directly polycondense it in the dispersed phase. This process is significantly faster than the regular PET synthesis processes, and allows one to obtain molecules with high molecular weights directly from a prepolymer without the need to use an intermediate solution polycondensation step. The prepolycondensation and SSP step are carried out in a slurry phase. The dispersant is a mixture of *n*-alkanes, composed primary of $C_{13}-C_{17}$ chains, with a boiling point of just over 250 °C [93].

DuPont de Nemours described another means of making polyesters in the patent literature [94—96]. This process, referred to as the NG3® Process, consists of making prepolymer particles of the order of a few millimeters in diameter, and crystallization in such a way as to leave it sufficiently reactive for the SSP.

Parashar and coworkers [97] reported step-growth swollen-state polycondensation (SwSP) applied for PET synthesis. The SwSP was carried out in a biphenyl and diphenyl ether solvent mixture (26/74 by mass) under appropriate conditions designed to take into account the factors responsible for enhanced reaction rates. The kinetics rate constants were found to be 2.5—5 times higher for SwSP as compared to SSP. As the diffusional/mass transfer effects were eliminated, the mobility of reactive chain ends increased.

CONCLUSION

Solid-state processes have already found application in obtaining of polymers on the technical scale such as aliphatic-aromatic polyesters (PET, PTT), aromatic polycarbonate and aliphatic polyamides. Besides esterification, transesterification and amidation also other types of reactions leading to high molecular weight polymers can be utilized in the solid-state processes. Oxidative-coupling as well as methathesis can be carried out according to the SSP mode, leading to poly(2,6-dihydroxy-1,5-naphthylene) and dialkoxy poly(phenylene vinylene), respectively.

Polymers obtained according to the SSP process are characterized by much higher molecular weight and higher thermal stability in comparison with those of polymers synthesized by melt polycondensation.

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