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On the Diffusion Mechanism in Melts of Condensation and Non-Condensation Polymers at High Temperatures

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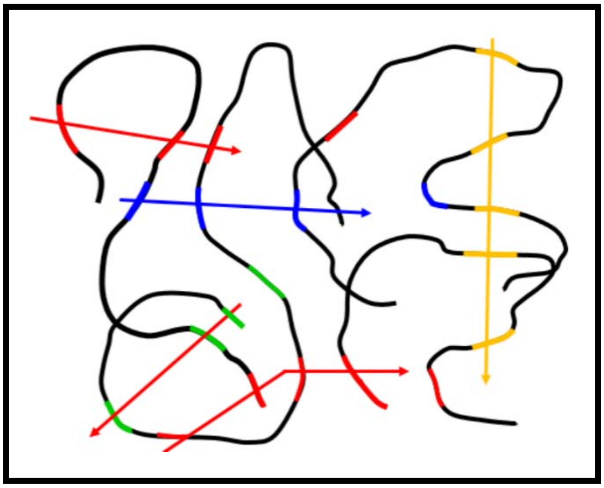
Graphical Abstract-



The experimental data regarding the frequency of exchange reactions in melts of condensation polymers show at least 10 reactions in a minute in one macromolecule (at low melt temperatures) and more than 100 reactions, but in a second (at high melt temperatures). At such temperature, the single independent kinetic elements are short fragments of macromolecules, and the diffusion mechanism in melts of condensation polymers seems to be the same, as that in the low molecular weight substances.

Keywords: diffusion mechanism; condensation polymers; exchange- (trans) reactions; reptation model.

I. INTRODUCTION

Diffusion is a physical process that refers to the net movement of molecules from a region of high concentration to one of lower concentration. The material that diffuses could be a solid, liquid or gas. In the case of solids some additional requirements are needed – the temperature must be above the melting temperature of the respective crystals or above the glass transition temperature of amorphous solids.

a) *The diffusion mechanism in low molecular weight substances*

The diffusion process in low molecular weight substances is well studied. Its basic characteristic feature is that independent kinetic entities are the whole molecules, that is, the whole molecules move but not parts of them only. The mass transfer could be represented as a process consisting of "jump-like" steps.

Let remind the picture of diffusion and flow in the case of low molecular weight liquids. If molecules have spherical shape, and they are densely packed, between the spheres (A) there are empty places (B), as shown in Figure 1. According to the ideas of Frenkel [1] the molecules vibrate with a given frequency. At some of vibrations the molecule "jump" in the neighboring empty place (e.g. A → B, Figure 1). After several vibrations around the new equilibrium state with the same frequency, the molecule "jump" again into another empty place. In this way is realized the process of self-diffusion of liquid molecules expressed in displacement of center of gravity of molecules, i.e. a flow takes place.

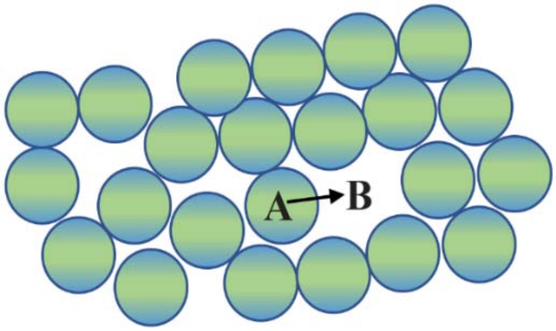


Figure 1: Schematic the packaging of spherical molecules in a liquid (A), and the non-occupied (free) volume (B)

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b) *The diffusion mechanism in high molecular weight substances*

The model shown in Figure 1 can be applied to polymer liquids (polymers in a molten state), at least partially, because the empty places are not big enough to accommodate the whole macromolecules comprised of many thousand linked atoms. In addition, a large amount of activation energy for displacement of whole molecules is needed. According to Eyring, it is 1/4 to 1.3 of the evaporation heat. If one summarizes this value for all repeating units of a macromolecule, one obtains a value which is much larger than the energy needed for breaking the chemical bonds leading to a chemical degradation of macromolecules. By the way, for the same reason the polymers do not exist in a gas state – before to evaporate the macromolecules decompose usually reaching the monomer state.

Solution of this situation can be found if we consider the fact that the independent kinetic units in macromolecules, particularly those comprised of flexible chains, are not the whole molecules but their segments. Then we can assume that the spheres in Figure 1 do not represent single molecules but segments of macromolecules, where between the segments there are also non-occupied places. What is more, for thermodynamic reasons, the number of these free places strongly increases with the rise of temperature. The more they are in a unit volume the more flexible are the molecules.

For flexible macromolecules it is possible the displacement of small sections of molecule without involving the rest of them, and for this are not needed large activation energies. It is experimentally proven when the growing molecule reaches the size of the segment, the activation energy of the viscous flow does not depend any more on the degree of polymerization. Just due to the subsequent displacement of small sections of macromolecule it is possible to move the whole molecule; the direction of this displacement is determined by the external force. It follows that polymer molecules moves not via "jumping" of whole molecule but via displacement of its small sections similarly to the movement mechanism of reptiles and worms.

The above-described model is applicable to polymers with not extremely high molecular weight, at least below their critical chain length, which for vinyl polymers equals twice the weight-average degree of polymerization. This limitation is related with the onset of entanglement and a modified model is required to account for the ability of long chains to translate and diffuse through the polymer matrix.

II. The "Reptation Model"

The problem of diffusion mechanism of large flexible chains was solved by de Gennes [2] and Edwards [3], who formulated the fundamental concept of *"Reptation model"*. In the de Gennes approach, the polymer chain is assumed to be confined in a hypothetical tube, the contours of which are defined by the position of the entanglement points in the network. In this way, the single polymer chain, trapped inside the "tube", is not allowed to cross any of the obstacles. This situation is presented graphically in Figure 2a. The macromolecules may move in a snake-like fashion among the obstacles, that is via *reptation* [2]. Lateral chain motion is severely restricted by the presence of neighboring chains. Mechanistically, reptation can be viewed as the movement of a "kink" in the chain along its length (Figure 2b). The amorphous polymers are the most often studied ones, as, for example, the polybutadiene because of its low glass transition temperature and high chain flexibility at room temperature.

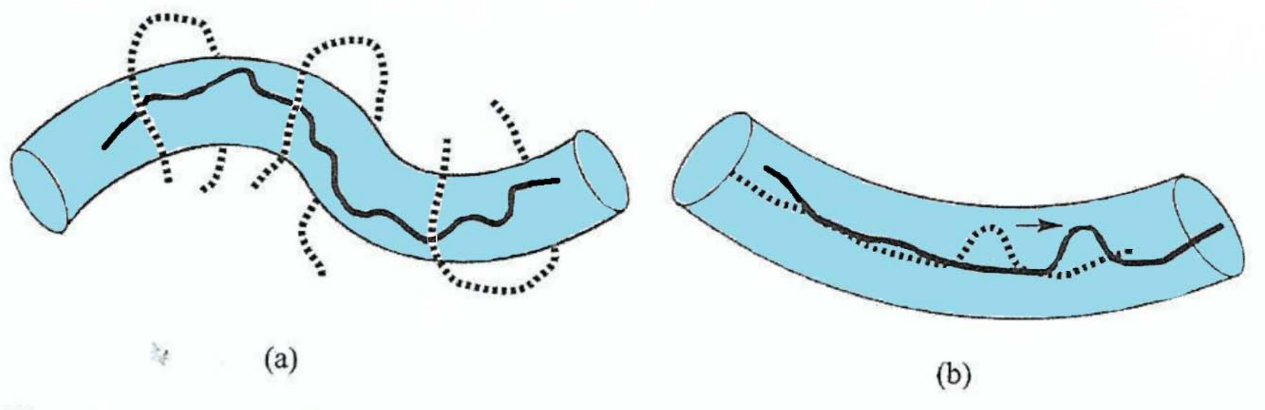


Figure 2: Schematic representation: a) – a polymer chain confined in a hypothetical tube contoured by fixed obstacles (depicted by dotted lines), and b) – movement of a "kink" along the chain until it reaches the end of the chain and leaves it. Successive motions of this kind translate the chain trough the tube and eventually take it completely out of the tube.

III. Further Development of the "Reptation Model" and its Criticism

In a quite early time [4] it was well understood that the mobility and self-diffusion of polymer molecules in concentrated systems or in the molten bulk state is largely controlled by entanglements between the molecules. These entanglements are a result of the chain-like nature of the molecules and of their extended, coil-like configuration. The conformation and mobility of polymer molecules in dilute solution, which are relatively simpler case, helped in consideration of self-diffusion in the more concentrated states and in the bulk polymer melt. The molecular self-diffusion controls several special properties of polymers as transport of biological macromolecules within living tissue, the morphology of semi-crystalline polymers and the flow properties of plastic melts - these are part of a broad spectrum of polymer properties controlled by the rearrangement and diffusion of polymer molecules.

Although the nature of polymers has been recognized for several decades, it is relatively later that a clear understanding of their self-diffusion in concentrated systems has begun to emerge. The physical picture is rather different to that associated with non-polymeric materials as mentioned in the Introduction. There are essentially two reasons for this: the sheer size of the molecules involved, and their intertangled nature. A typical polymer molecule consists of several thousand monomer molecules, connected as a long flexible chain; in addition, it may adopt an exceptionally large number of different configurations, because there is, generally, easy rotation about the backbone bonds [5]. In the bulk material, this chain folds up in the form of a loose coil, occupying a volume many times that of the chain itself. Since the volume of the coil not occupied by the chain is nonetheless filled with polymer, it follows that any given polymer molecule is interpenetrated by, and intertangled with other molecules very intimately. Because of this, a polymer chain cannot diffuse by random thermal hops in which it moves as a single unit, as is essentially the case with smaller molecules and atoms as described above. Its translational motion, rather, and the way in which it disentangles itself from its neighbors, are cooperative processes, which represent the sum of random motions of all monomers along the chain; a polymeric molecule may thus be subject to long-range interactions - such as entanglements, which small molecules do not experience [4].

Fundamental contributions to the development of the ideas of self-diffusion in polymer melts have done by L. Leibler, M. Rubinstein and R. Colby covering polymers with various architecture, structure, composition, and other characteristics (e.g. [6-16]).

A peculiarity of almost all studies on relaxation and self-diffusion of a polymer chain in a melt is that these studies concern exclusively non-condensation polymers, typically polyolefins. To them belong hydrogenated polybutadiene used for evaluation of the self-diffusion coefficient in its melt [17], polyethylene and polystyrene, used for studying the molecular weight and temperature dependence of self-diffusion coefficients [18]. Stars, combs, rings, and polydisperse samples have been used to get a new information on diffusion mechanisms [19].

The self-diffusion coefficient and zero-shear viscosity have been measured in the melt state for a series of three-arm star hydrogenated polybutadienes [20]. Poly (vinyl) acetate-toluene and Neoprene-acetone have been used for evaluation of the diffusion coefficients in polymer-solvent systems for highly concentrated polymer solutions [21].

Self-diffusion and tracer diffusion of hydrogenated and deuterated polybutadienes, both above the entanglement molecular weight have been investigated over a broad range of molecular weight to study the reptation and constraint release in linear polymer melts [22].

In the rather rare publication on polyesters [23] the growth of branched polymer structures up to the gel point has been examined a polyester system at two different branch agent concentrations. In all cases, scaling relationships between various properties were displayed for the whole range of molecular weights [23].

In a review on the tube theory of entangled polymer dynamics [24] it is stated that the dynamics of entangled flexible polymers is an appealing interdisciplinary field where experimental and theoretical physics can work closely with chemistry and chemical engineering. Further on, the role of topological interactions is particularly important, and has given rise to a successful theoretical framework: the "tube model". In the same review are discussed specially synthesized model materials, an increasing palette of experimental techniques, simulation and both linear and nonlinear rheological response. It is concluded [24] that our current understanding of a series of processes in entangled dynamics: "reptation", "contour length fluctuation" and "constraint-release" are set in the context of remaining serious challenges. Especial attention is paid to the phenomena associated with polymers of complex topology or "long chain branching".

Even stronger effects of molecular topology on diffusion have been observed for entangled DNA molecules [25].Among polymers, DNA is rather unique in that it is naturally found in several different topological forms, including linear, supercoiled circular, relaxed circular, knotted circular, and branched. When long polymers such as DNA are in a highly concentrated state, they may become entangled leading to restricted self-diffusion. The effect of molecular topology on diffusion in concentrated DNA solutions was investigated and surprisingly large effects were found. It was concluded that the diffusion in entangled DNA solutions strongly depends on topology of both the diffusing molecule and the surrounding molecules [25].

The same problem, namely the entangled polymer dynamics beyond reptation was recently [26] treated in detail. For this purpose, linear and cyclic ds-DNA molecules as model system was used, and a new single-molecule characterization platform by combining super-resolution fluorescence imaging and recently developed single-molecule tracking method, cumulative-area tracking, which enables to quantify the chain motion in the length and time scale of nanometers to micrometers and milliseconds to minutes.

It is manifold demonstrated that the rheological properties of polymer materials microscopically arise from entanglement of polymer chains [2,3]. Decades of theoretical, experimental [27-32], and simulation studies [33-35] suggested that topological states of polymer (e.g. linear, cyclic, etc.) have significant effect on entanglement mode between the chains [36]. Recent studies demonstrated that the topological states of polymer chain are one of the key factors that regulate macroscopic physical properties of polymer materials, including thermal stability of polymer micelles [37,38] and elastic properties of polymer gels [39]. Nanoscopic characterization of the entanglement between topological polymers at the single-chain level would thus provide a foundation for the development of new polymer material.

Motion of a linear polymer chain under entangled conditions has been described by reptation theory [3]. In this theory, as already mentioned, a polymer chain is confined in a transiently existing virtual tube created by entangled surrounding chains. Due to this spatial confinement, the chain cannot move transversely across the tube and displays motion only along the tube as can be concluded from Figure 2. According to this model, motion of the entire chain is determined by the motion of two ends of the chain. It is obvious that the reptation theory cannot fully describe the motion of topologically unique cyclic polymer chains under entangled conditions as cyclic chains do not have chain end [26]. Several theoretical frameworks describing motion and relaxation of entangled cyclic chains have been proposed, including double-folded-reptation, lattice-animal, constraint release, and once-threaded model [40-44]. Contribution of mutual relaxation between entangled chains and decoupling of diffusive motion and chain relaxation on entangled cyclic polymer dynamics have also been suggested [45,46]. Compared with well-accepted reptation model for linear polymers, cyclic polymer dynamics remains elusive [26].

Nuclear magnetic resonance spectroscopy, light and neutron scattering, and viscosity and stress-relaxation measurement have been main tools for characterizing polymer dynamics [47-49]. Reptation model has been confirmed for linear chains using natural polymers such as DNA [50] and actin filament [51] as well as synthetic polymers [52]. In these studies, although motion and conformational state of single chain were captured directly, quantitative analyses were often conducted based on overall motion and relaxation of the chains such as chain-length-dependent motion of center of mass [26].Using this new method [26], it was demonstrated that the motion of the linear chains under entangled conditions occurring at the level of both whole chain and entangled segment are consistent with the reptation model. The results obtained suggest also that the motion of the cyclic molecule at the whole chain level is distinct from that of the linear chain because of the topological constraint of the cyclic chain under entangled conditions rather than topology-dependent local chain motion and interaction. It was also proved the existence of hypothesized but unproven modes of the motion of cyclic chains under entangled conditions, including amoeba-like motion of double-folded loop-like region [26].

From this brief review of the development of the reptation theory it could be concluded that the Reptation model can be applied for explaining the self-diffusion mechanism of polymers comprised of flexible chain-like macromolecules, which preserve their chemical composition (even at elevated temperatures, e.g. their melts) during the diffusion process, that is, the diffusion is not paralleled by chemical reactions. The non-condensation polymers inherently fulfilled these characteristic requirements. On the contrary, the condensation polymers are distinguished by chemical peculiarities, which make the application of Reptation model for describing the diffusion in their melts questionable. The subsequent sections of this review deal with the chemical peculiarities of condensation polymers, which could help us in answering the question regarding application of Reptation model to the melts of condensation polymers for explaining of their diffusion mechanism. Finding of this answer is just the target of this study. An additional reason for treating the condensation polymers in this respect is the fact that the reptation theory was supported by experimental results from studies of exclusively non-condensation polymers.

IV. The Chemical Peculiarities of Condensation Polymers [53]

At the beginning let remind a basic knowledge in the polymer science. Polymers are synthesized mostly by two chemical reactions: polycondensation and polymerization. In the first case the functional groups (e.g. -COOH, -OH, $-NH_2$, and others) of the monomers react and a low molecular weight product (usually H_2O) is separated. In the second case the reaction goes via opening double or triple bonds, or cycles and no low molecular weight product is separated.

Another basic difference between the two processes is the fact that in the case of polycondensation, at the ends of the formed macromolecules remain functional groups capable to react further if the respective conditions are available.

In the case of polymerization such an opportunity is missing (a rare exception is the “living” polymerization). The two basic chemical reactions for polymers synthesis look like this:

Polycondensation:

$$\mathrm{HOOC\text{-}R\text{-}COOH + HO\text{-}R'\text{-}OH} \rightarrow \underset{\text{polyester}}{\mathrm{HO(\text{-}OC\text{-}R\text{-}COO\text{-}R'\text{-}O\text{-})H}} + \mathrm{H_2O} \qquad (1)$$

Polymerization:

$$n\mathrm{CH_2{=}CH_2} \rightarrow \underset{\text{polyethylene}}{(\mathrm{\text{-}CH_2\text{-}CH_2\text{-}})_n} \qquad (2)$$

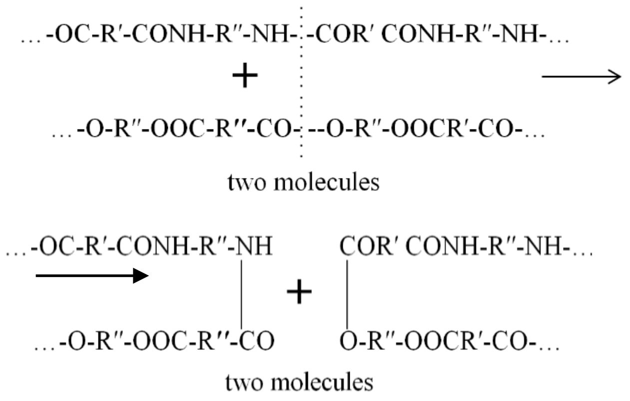
Some polymers, regardless of their type of synthesis, contain as side groups various functional groups (-OH, -NH_2, -COOH and others), which can undergo chemical reactions with similar groups of another polymer if the respective reaction conditions (heat, catalyst, vacuum, etc.) are present. These reactions have the specificity that they do not involve the backbone of macromolecules but their side groups only [5].

The condensation polymers, in addition to this type of reactions, can realize also chemical interactions with the participation of backbone atoms [54,55]. The most typical are the *trans- (exchange-) reactions* and the *additional polycondensation*:

Additional polycondensation:

$$\underset{\text{two molecules}}{M_n + M_m} \;\rightarrow\; \underset{\text{one molecule}}{M_{n+m}} \qquad (3)$$

Trans- (exchange-) reactions:



(4)

These reactions take place during the heat treatment of linear polyesters or polyamides (as well as their blends) at elevated temperatures (close to the melting point – above or below!), particularly in vacuum or in an inert gas flow. The additional solid-state condensation involves the chain-end groups, and the transreactions - the near situated intrachain- or interchain-groups.

The basic difference between the described two types of reactions, (eqs. (3) and (4)) is that in the case of additional reactions two macromolecules yield only one new macromolecule, (eq. (3)), while in the transreactions the starting two macromolecules form two new ones, each of them comprising a part of each of the reacting chains, (eq. (4)). Eventually, the additional polycondensation is accompanied by an increase of the molecular weight in contrast to the transreactions, in which the average molecular weight is unchanged [5,54,55]. Further on, the transreactions lead to formation of block copolymers (e.g. polyesteramides, as shown in the above example, eq. (4)) if the reacting macromolecules differ in chemical composition.

For a couple of decades, the solid-state postcondensation has been a well-known process [55-60] particularly in the case of poly(ethylene terephthalate) (e.g. [61]). The effect of numerous factors (temperature, duration, particle size, medium, etc.) on the molecular weight increase for polyesters and polyamides has been intensively studied and described mainly in the patent literature, because of the technological importance of this process.

Exchange reactions of polyesters are usually carried out in a molten state (ca. 5-10 °C above T_m). It has been shown by careful investigation [62] that ester interchange reactions of poly(ethylene terephthalate) (PET) can take place 20-30 °C below T_m, e.g., in the solid state. In the solid state, the rate of reaction of this polymer becomes relatively high at temperatures above 225 °C and is catalyzed by the free carboxylic end groups of the polyester [62].

a) *The additional (post) polycondensation and the exchange- (trans) reactions in polymer science and technology*

Among the condensation polymers, possibly, the most important are the polyesters and polyamides (Nylons). This is related with their first and very wide application as textile and technical fibers. Some later, particularly the polyamides, were applied as engineering plastics and during the last 2 - 3 decades PET found a large application as packaging material (mostly for bottles of pressurized soft drinks). It turned out that PET is non-replaceable material in this respect due to its transparency, chemical resistivity, gas and vapor non-permeability, light weight, and others, and for these reasons it enjoys 10% annual increase in its production [63].

Discussing these three rather different areas of applications of condensation polymers it seems important to mention that for each of these cases one must apply a different processing technique: fibers are produced by spinning, engineering plastics – via injection molding, and PET bottles – by means of injection molding and extrusion. For the spinning process one needs polymers with molecular weight around 20 000 because their melt viscosity corresponds to the required viscosity for performing of spinning process. Luckily, this is the molecular weight of the polycondensates after their primary synthesis. For using the injection molding, and particularly the extrusion, for processing the same polymers much higher melt viscosities are needed. Unfortunately, they cannot be reached during the primary synthesis of polymers because of the drastic increase of melt viscosity making further stirring of the reaction mixture impossible.

The solution of the problem has been found in using one of the chemical peculiarities of condensation polymers – their ability to undergo additional (post) condensation even in a solid state, as mentioned above. On the commercial importance of these reactions firstly stressed Flory in the mid-thirties of last century [55] and later described in the open (e.g. [64]) and mostly patent literature because of its commercial relevance.

The additional condensation in solid state is carried out with chips synthesized for fiber production in a reactor (usually under vacuum) at temperatures close but below melting for a couple of hours. Obviously, the importance of the solid-state additional condensation will steadily increase since the increasing needs of packaging materials – because of bad packaging 50% of the food in the developing countries is spoiled, while in UK this amount is 2-3% [65].

The exchange reactions between condensations polymers also play a significant role in polymer science and technology. Let mention the case of polymer-polymer composites only. The mechanical performance of composite materials depends primarily on the adhesion quality on the interface between the matrix and reinforcement for effective transfer of the load between the two-basic component of the composite. In case these components represent condensation polymers, due to the exchange reactions an ideal adhesion is realized because of establishing chemical bonds between the matrix and reinforcement (e.g. [66, 67].

Quite similar is the case with the compatibilization phenomenon in polymer blends and polymer-polymer composites involving condensation partner. Since by far the most of polymer pairs are thermodynamically non-miscible, for improving of their compatibility a third component, a “compatibilizer” is used, similarly to the surfactants in low molecular weight mixtures. A good example in this respect is the malleated polypropylene (PP) used in blends and composites of PP with polyesters and polyamides. Maleic anhydride undergoes to trans-reaction with the condensation partner (e.g. [68, 69]).

b) *Chemical healing in condensation polymers*

Self-healing is a well-known phenomenon in nature. The concept of “self-healing” of synthetic materials emerged a couple of decades ago and continues to attract scientific community progressively [70-79]. Self-healing polymers and fiber-reinforced polymer composites possess the ability to heal in response to damage wherever and whenever it occurs in the material. To date, self-healing has been demonstrated by three conceptual approaches: capsule-based healing systems, vascular healing systems, and intrinsic healing polymers [70, 71].

In a recent [80] detailed review on the chemical and physical aspects of self-healing materials it is stated that “*Due to limited chain mobility and a lack of bond reformation abilities, common polymers do not show self-repair attributes*” [80]. How does look the situation in reality?

When two samples of the same amorphous polymer are brought into good contact at a temperature above the glass transition, the interface gradually disappears, and the mechanical strength of the polymer-polymer interface increases until, at long contact times, the full fracture strength of the bulk polymer is regained. At this point the junction surface has become in all respects indistinguishable from any other surface that might be located within the bulk material - the junction has “healed.”

The earliest systematic studies of healing in polymers were related with autoadhesion (direct bonding or self-bonding) and adhesion of polymers [81] undertaken by Voyutskii [82], who proposed a molecular interpretation based on the diffusion of macromolecules. Some later, around 80-ies of the last century, the crack healing in polymeric materials has been a subject of intensive investigation summarized in recent reviews [81, 83-85]. To the same period belongs the formulation of the fundamental concept of "Reptation model", done mostly by de Gennes [2] and Edwards [3]. Their idea was immediately implemented in the molecular interpretation of the healing process [80, 81, 83]. The amorphous polymers are the most often studied ones. The crack healing is modeled at microscopic level by the following healing parameters: (i) center-of-mass Fickian interdiffusion in the healing of elastomers, (ii) average chain segment displacement and formation of new entanglements in the interfacial regions, (iii) change in crossing density of molecular chain end [80,83].

The self-diffusion in a bulk polymer helps to understand the healing process in the best way, but the two processes are not identical [83]. In the case of self-diffusion, the coils move over distances many times their mean diameter, whereas healing is essentially complete in the time it takes a polymer molecule initially next to the junction surface to move halfway across it. The healing time may take minutes, hours, or even days depending on the healing temperature and polymer characteristics [83]. Configurational relaxation in the bulk polymer is usually described by the "Reptation model" [2,3].

The described cases of self-repairing could be called *physical healing* so far one deals with samples which have not been subjected to any chemical treatment prior or during the healing process. An additional reason to precise the terminology is the fact that around the same time (1984) it was demonstrated that self-repairing is possible also because of chemical reactions in the same one- or two-component chemically non-treated polymers [86].

This was possible because a special attention was paid to linear condensation polymers. Like other classes of polymers, their chain flexibility increases with increasing temperature. Besides this physical process during the heating, as mentioned foreheads, chemical changes are also possible. In addition, the diffusion of low-molecular-weight fractions to the surface is a well-known phenomenon for poly(ethylene terephthalate). Such an enrichment of the surface on reactive chain-end groups will enhance the chemical reactions on the surface. It seems quite reasonable to expect that these reactions could take place at the interface between two samples of polycondensation polymer if (i) the contact is good enough, and (ii) suitable reaction conditions are created [86].

This assumption is supported by the observation mentioned above [62] that ester interchange reactions of poly(ethylene terephthalate) take place 20-30°C below T_m, that is, in the solid state.

The new molecular mechanism for the healing phenomenon in semicrystalline linear polycondensates, that is healing resulting from chemical reactions between macromolecules located in the interfacial surface, has been demonstrated by means of strips of commercial PET film. They have been annealed at 258°C to increase their T_m up to 260 – 268°C thus avoiding melt sticking during the subsequent heat treatment [86]. Two such strips are partially overlapped as shown in Figure 3, pressed, and heated in a vacuum at 240°C for 10 to 100 h. By measuring the stress at break, σ_b, outside the contact area and the debonding shear stress, τ_i, the critical overlapping length, l, has been computed. Further experiments [87] lead to the conclusion that transreactions contribute more than solid-state post condensation to the chemical healing.

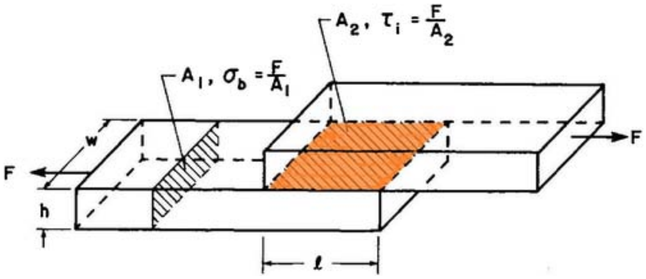


Figure 3: Schematic geometry of samples used for chemical healing experiments: σ_b – tensile strength, τ_i – shear strength [86]. Source: Fakirov S. Chemical healing in poly(ethylene terephthalate). Journal of Polymer Science: Polymer Physics Edition, 22, 2095–2104 (1984). Copyright 1984 John Wiley & Sons, Inc.

If two linear condensation specimens are undergoing the stage of wetting [80, 83], and the temperature is high enough, the solid-state post condensation and interchange reactions start. They result in the completion of the last two stages (diffusion and randomization) [80, 83]. An interesting assumption could be formulated in this case, namely, that to achieve a given extent of recovery, the "*chemical*" healing needs less time than the "physical" one. There are at least two reasons for this: (i) the "chemical" healing is less diffusion controlled (the most important factor seems to be the perfection of the contact) and (ii) the chemical interaction is possible even in the amorphous areas of the crystalline regions, as schematically represented in Figure 4. The diffusion (e.g., mutual interpenetration of the chains) is considered only in amorphous regions (Figure 4.), which for PET represent less than 50% of the surface [86].

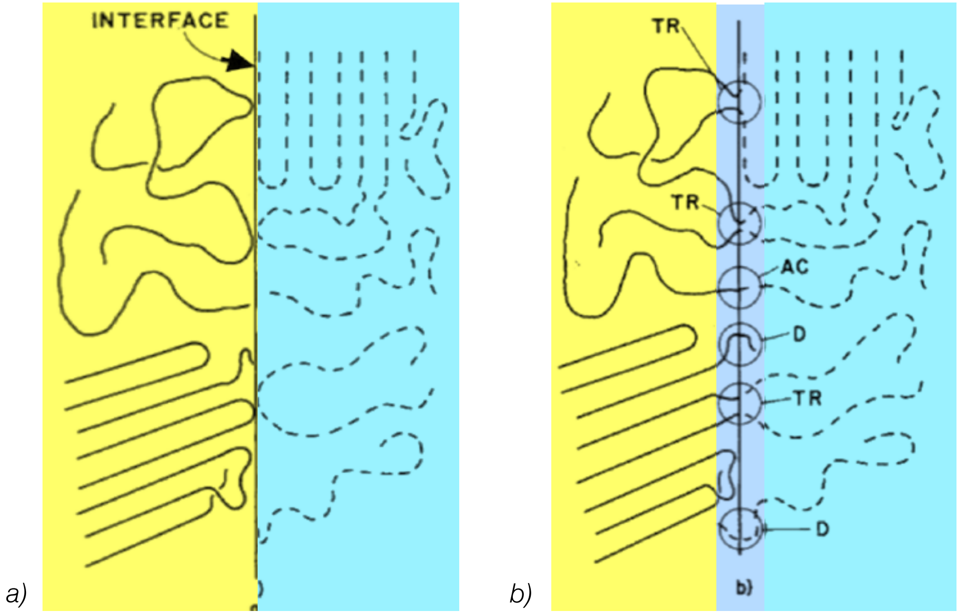


Figure 4: Schematic of chemical healing process in a semicrystalline linear polycondensate at temperature close (but below) to the melting: (TR) -transreaction, (AC) - additional condensation, (D) - diffusion [86]. Source: Fakirov S.: Chemical healing in poly (ethylene terephthalate). Journal of Polymer Science: Polymer Physics Edition, 22, 2095–2104 (1984). Copyright 1984 John Wiley & Sons, Inc.

Summarizingit could be concluded that the experiments described demonstrate a new molecular mechanism of the healing phenomenon in semicrystalline linear polycondensates - healing because of chemical reactions between neighboring macromolecules located in the interface surface. To distinguish this case of self-repairing from the previous case, the physical healing, it has been suggested [86] to be called *chemical healing*. Evidently, the chemical healing is quite a general property for all condensation polymers characterized by the ability to undergo transreactions and/or additional condensation. R. Porter [68] has acknowledged this fact in his review on compatibility and transesterification in binary polymer blends as well as done in the recent monography of H. Kricheldorf [54] on polycondensation.

The common characteristic feature between the physical healing and the chemical healing is the fact that they are observed with chemically non-treated or modified polymers. The self-repairing in these two cases is related with the two basic and inherent properties of macromolecules – the ability to diffuse as well as to undergo chemical reactions (for condensation polymers only!). It seems quite reasonable to call just these two cases of self-repairing "*self-healing*", since the respective polymers have not been subjected to any chemical treatment before performing the healing procedure or during their primary synthesis by adding a specific comonomer.

At the same time, in the last decade it has been noted that a few classes of reactions (currently they are at least 15 types [88]) offer self-repairing through the cleavage and reformation of specific bonds [80] but these cases hardly could be called "self-healing". The reason for this statement is that to perform this type of healing the respective polymer must be subjected to specific chemical treatment or during its basic synthesis a special comonomer must be used. Possibly, for such cases of self-repairing it would be more accurate to use the term *"chemically assisted healing"*.

The importance of the lack of external chemical intervention in proceeding of the self-healing processes is supported also by the interpretation of the term itself. According to Cambridge dictionary, "self-healing" means "*to describe a piece of equipment or system that has the ability to discover and correct faults without needing outside help".*

Discussing the terminology aspect of the self-repairing phenomenon, one must add that the above-described case of chemical healing with condensation polymers could be further specify as *homochemical healing* [86,87] since it has been demonstrated [89] that chemical healing can be observed also if two chemically different condensation polymers are subjected to healing procedure. In such a case one deals with *heterochemical healing*. Such type of healing has been observed on two pairs of samples – PET and Nylon 66 as well as poly (butylene terephthalate) (PBT) and Nylon 6 [89].

All the above-described experiments on chemical healing [86, 87, 89] have been performed with polyesters and polyamides characterized by relatively good chain mobility. To distinguish the contribution of physical from chemical processes similar experiments have been carried out with polymers known by their inherent strongly restricted molecular and segmental mobility due to the great rigidity of their macromolecules, as for example the case with cellulose is [90]. Multi-layered sheets of cleanex (fibrous delignified native cellulose) have been annealed at temperatures between 120 and 265°C under or without pressure. The tensile testing demonstrated that the strength is four times and modulus – eighteen times higher for the pressed sample than the non-pressed ones. A conclusion is drawn [90] that the observed welding cannot be attributed to diffusion of macromolecules through the interface; it is due mainly to solid state chemical reactions at the contacting surfaces. It should be mentioned that this same conclusion led to the healing experiments with a liquid crystalline polymer [91].

Further on, an attempt has been made to evaluate in a more precise way the contribution of solid-state chemical reactions to the healing effect between two contacting bulk pieces via chain mobility restrictions on a series of polyamides (Nylon 11, Nylon 12, and Nylon 66) [92]. Strips with higher melting temperatures have been obtained by annealing. To suppress the chain mobility in amorphous regions and to exclude or greatly minimize the diffusion of macromolecules during the healing process, the samples have been partially (only in amorphous regions) cross-linked using the technique of Arakawa et al., [93] based on methoxy methylation.

After such pretreatment of the samples the healing procedure is performed with partially overlapped strips (Figure 3) at temperatures enough below their respective melting to avoid sticking. Since at these healing temperatures the chains in crystallites are also immobilized, one can conclude that the observed welding effect is due exclusively to the chemical reactions on the contact surfaces.

The best proof for the dominant role of the solid-state chemical reactions in the healing process in linear condensation polymers is the observation that under the same healing conditions, the cross-linked samples of Nylon 11 display much higher shear stresses than un-cross-linked ones. It should be added that with cross-linking the shear modulus also changes, which affects the shear stress. If the diffusion of macromolecular chains is the controlling factor in the healing, then dealing with cross-linked samples one must observe the reverse situation [92].

A common characteristic feature of transreactions and the additional condensation regarding the healing effect is that they are possible only if the reaction partners are close enough in the space. Further on, if one considers that the concentration of the partners for transreactions is much higher than that of the terminal groups and that crystallinity and cross-linking suppress mobility, it follows that the probability of collision of the terminal groups is drastically reduced. At the same time crystallization and cross-linking lead to an increase in the rate of transreactions, due to an increase in the concentration of stressed contact points [95]. In such a situation, the transreaction processes are favored, and it can be concluded that the healing effect is mainly a result of transreactions [92].

As a matter of fact, the most serious support in favor of conclusion about dominating role of chemical reactions in self-repairing process are the healing experiments with polyimide films characterized by extremely high values of their glass transition temperatures, T_g [96]. For example, T_g of Upilex-R (polyimide) is 285°C, and that of Kepton-H (polypiromellitimide) – between 360 and 410°C. The healing experiments have been performed in the way described above for other polymers, as well as their testing. The applied healing temperature (T_h) has been 250°C, that means below or far below their T_g-values. The selected healing temperature has two important peculiarities: (i) it is high enough for performing of chemical reactions, and (ii) it is not high enough for realization of molecular movement since the respective polymer is at temperature below its T_g where such movement is excluded.

A jump in the temperature dependence of the shear stress of Kepton-H and Upilex-R is worth mentioning. The increase of the activation energy could be explained by chemical reactions taking place at the contacting surfaces [96].

The fact that the healing process is carried out at temperatures below the glass transition temperature of the respective polymer where the molecular diffusion is excluded, gives an idea about the contribution of the physical processes to the healing, that is, the welding in this case is due exclusively to the chemical processes [96].

c) *Sequential reordering in condensation copolymers via transreactions*

The study of transreactions started with the pioneering work of Flory [55]. These reactions have been convincingly confirmed, as mentioned in the previous sections, by studying blends of protonated PET with deuterium labelled (d4) PET by SANS; they take place rapidly in the melt as well as at lower temperatures (some 20-30°C below the melting of PET [62]) resulting in formation of a block copolymer [97]. In the subsequent years they have been widely used for preparation of condensation copolymers starting from blends of homopolymers (e.g. [98]). The blends are converted first into block copolymers and finally into random copolymers because all repeating units are equally likely to react. Therefore, the properties of a blend in which transreactions are possible depend on the rate and degree of completeness of exchange reactions.

In fact, any type of sequential order is characterized by the properties, mostly physical ones.

For example, a copolymer with blocky sequential ordering should crystallize if at least one of the starting homopolymers is crystallizable and that a copolymer with random type of sequential ordering is non-crystallizable. The study of the behavior of the crystalline phase(s) can offer an insight in the occurrence and depth of chemical interactions between the blend components as well as in the sequential order in copolymers. At the same time, the properties of the amorphous phases will support these conclusions since at the stage of complete randomization, particularly in equimolar blends of condensation polymers, a single glass transition should be observed instead of the two glass transitions, typical of a mechanical blend or of a block copolymer as shown in Figure 5.

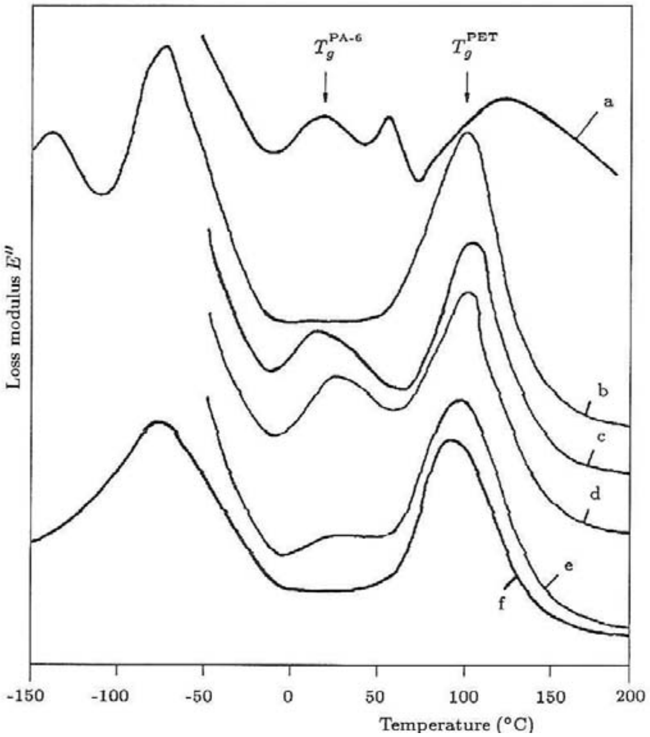


Figure 5: Temperature dependence of the loss modulus E'' in the range from -150 to 200°C. Annealing temperatures and durations are as follows: (a) non-annealed, undrawn; (b) non-annealed) drawn to λ= 4.2; (c) T_a= 220°C, t_a= 5h; (d) T_a=220°C,t_a=25h;(e)T_a=240°C, t_a= 5h;(f)T_a=240°C,t_a=25h [99]. Source: Serhatkulu T., Bahar I., Erman B., Fakirov S., Evstatiev M., Sapundjieva D.: Dynamic mechanical study of amorphous phases in poly (ethylene terephthalate)/nylon-6 blends. Polymer, 36, 2371–2377 (1995). Copyright 1995 Elsevier.

The method of dynamic-mechanical thermal analysis (DMTA) is commonly considered as the most reliable technique for the determination of T_g and for this reason it was applied to the PET/PA 6 blend subjected to drawing and annealing. The results are summarised in Figure 5 [99].

Again annealing at lower temperatures, or at higher ones (240°C but for shorter times), leads to the formation of two well-defined and spatially separated amorphous phases, characterized by two glass transition temperatures, T_g^{PET} and T_g^{PA6} for the PET and PA 6 amorphous phases, respectively (Figure 5c,d). Annealing at 240°C for 5 h (Figure 5e) results in a decrease in the PA 6 amorphous fraction. After annealing for 25 h it disappears completely (Figure 5f). This observation indicates that after such a thermal treatment, all of the amorphous PA 6 is involved in a copolymer with the amorphous PET.

Evidence derived from the behavior of the crystalline phases has been obtained on the same blend of PET with polyamide 6, subjected also to drawing after extrusion and annealing for various times around the melting temperatures of the blend components [100]. Wide-angle X-ray scattering (WAXS), Figure 6, demonstrates that the thermal treatment at 220°C for 5 h (Figure 6a) results in a crystalline highly oriented polymer blend. The situation changes drastically after annealing at 240°C for 5 h (Figure 6b) - the PA 6 diffraction patterns are in the form of Debye rings, suggesting isotropy of that component. At the same time, the orientation and perfection of the crystallites in the PET fraction remain unchanged. Prolonged annealing (25 h) at the same temperature (above T_m of PA 6!) leads to the almost complete disappearance of the PA 6 Debye rings (Figure 6c).

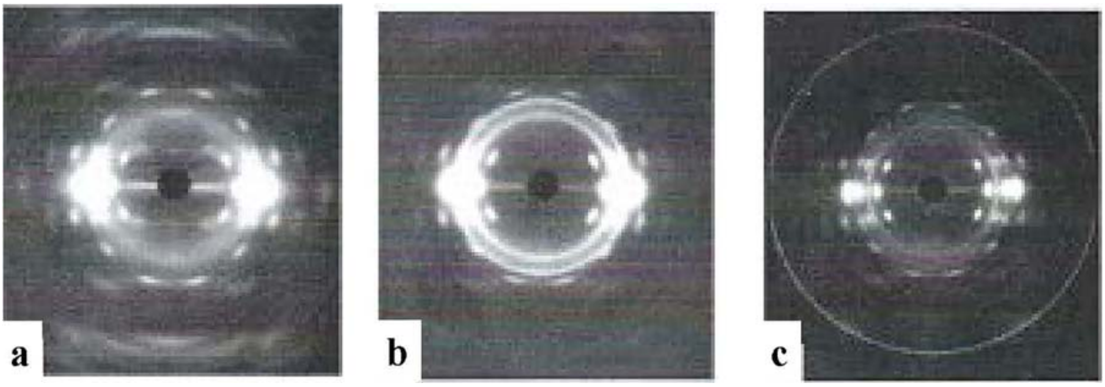


Figure 6: WAXS transmission patterns of PET/PA 6 blend, zone-drawn and annealed at different temperatures and for various durations: (a) T_a=220 °C, t_a=5h, (b) T_a=240 °C, t_a=5h, (c) T_a=240 °C, t_a=25h. The patterns are taken at room temperature after the respective annealing [100]. Source:Fakirov S., Evstatiev M., Schultz J. M.: Microfibrillar reinforced composite from drawn poly(ethylene terephthalate)/nylon-6 blend. Polymer, 34, 4669–4679 (1993). Copyright 1993 Elsevier.

The WAXS patterns shown in Figure 6 also demonstrate an important peculiarity of transreactions in condensation polymers – they take place even if one of the reaction partners is in a solid state. The annealing temperature of 240°C is by 20°C above the T_m of PA 6 and at least by 15°C below the T_m of PET. If at this temperature PET is in a molten state it should lose its orientation as PA 6 did during the shorter annealing at 240°C (Figure 6b). Figure 6c proves that PET preserves its orientation during annealing at 240°C, that is, it remains in a solid state. On the possibility of performing of chemical reactions in a solid PET (some 20°C below melting) was indicated even earlier [62].

What is more, the same data from WAXS (Figure 6c) and from DSC (Figure 7, curve (f)) demonstrate that the total amount of PA 6 react with the half of the PET only since the other half builds the crystallites, which are not involved in the chemical interactions (typically, the maximum crystallinity of PET is 50%).

To the same conclusions leads the testing of the same samples by means of differential scanning calorimeter (DSC) [100] as demonstrated by the respective curves displayed in Figure 7.

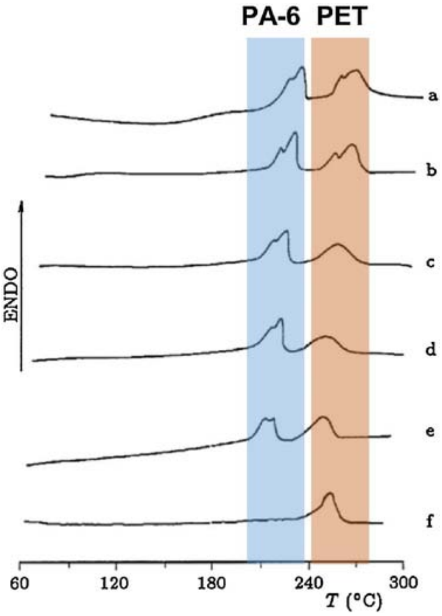


Figure 7: DSC curves of PET/PA 6 blend (ultraquenched, zone-drawn and additionally annealed at different temperatures and for various durations) taken in the second heating mode. Annealing temperatures T_a and durations t_a: (a) unannealed, undrawn; (b) unannealed, drawn 4x, (c) T_a=220 °C, t_a=5h, (d) T_a =220 °C, t_a=25h, (e) T_a =240 °C, t_a=5h, (f) T_a =240 °C, t_a=25h [100]. *Source*: Fakirov S., Evstatiev M., Schultz J. M., Microfibrillar reinforced composite from drawn poly(ethylene terephthalate)/nylon-6 blend. Polymer, 34, 4669-4679 (1993). Copyright 1993 Elsevier.

These observations indicate that after such a thermal treatment, the total amorphous PA 6 is involved in a copolymer with the amorphous PET. The behavior of both, the crystalline (Figures 6 and 7) and amorphous [99] phases clearly indicates that the PA 6 starting component does not exist anymore as individual component. This is due to its involvement in a copolymer with a supposedly random structure because of transreactions taking place during prolonged annealing at elevated temperatures.

It should be mentioned that the described chemical changes are proven also by following the behavior of other physical properties during melt annealing at various temperatures and durations. For example, application of IR spectroscopy after selective extraction with formic acid, accompanied by weight control of the fraction supports the above conclusions. The weight loses after extraction are given in Table 1.

Table 1: Weight loses (based on the PA 6 content) as a result of selective extraction of PA 6 of a PET/PA 6 blend (1:1 by wt.) after various thermal treatments [100]

	Samples as in Figure 7					
	a	b	c	d	e	f
Annealing temp. (°C)	-	-	220	220	240	240
Annealing time (h)	-	-	5	25	5	25
Weight loss (%)	98	96	91	80	62	22

However, the losses depend strongly on the annealing temperature - for the thermally untreated samples they are about 100% whereas after annealing at 240°C for 25h they drop to about 20% (Table 1, samples (a) and (f)). It can be concluded that practically the entire PA 6 fraction is extracted in thermally untreated samples, in contrast to those annealed at 240°C for 25 h. The rise in the intensity of the IR absorption band at 3300 cm^{-1}, as well as in the range of 2200- 2800 cm^{-1}, which is characteristic of the vibrations of the $-CH_2-$ groups, follows the same trend since the copolymer is enriched in $-CH_2-$ groups, as compared to homo-PET [102]. Thus, it is quite clear that the amount of PA 6 incorporated in a copolymer increases with the rise of the annealing temperature and duration.

The involvement of the total starting amount of PA 6 into a copolymer with PET has been demonstrated also by selective (only PA 6) dying with wool-type dyestuff – a complete homogeneous dying of the thin slices on the microphotographs after the final treatment is observed, contrasting the partial dying in the non-treated samples [101].

The exchange reactions and particularly the sequential order in condensation copolymers prepared via interchange reaction in blends of condensation homopolymers have been studied by Lenz et al. (e.g. [103], Devaux et al. (e.g. [104]), Economy et al. [105,106] and others. The first systematic study on the factors determining the sequential order in these copolymers has been performed by Fakirov et al. (e.g. [107]). These studies ([107]) have been based on the understanding that the exchange reactions resulting in randomization of the copolymers are the same as those leading to regeneration of the blocky character of the copolymers, that is, the sequential order is not determined by the exchange reactions but by other factors present in the system at the given conditions. The exchange reactions are a tool only for realization of one or other sequential order, they do not determine this order! About the type of the sequential order in these studies (e.g. [103]) it has been judged exclusively from the crystallization (T_m) and glass transition (T_g) behaviors.

What is more, using these factors it is possible to control the sequential order in condensation copolymers as it will be demonstrated below.

i. *Melting-induced sequential reordering in condensation copolymers*

The clearest case regarding the factors determining the type of the sequential order is that of the melting-induced sequential reordering. It is generally accepted that because of direct interchange reactions, the blend of homopolymers transforms into a block copolymer which subsequently turns into a random one:

$$(A)_n + (B)_m \rightarrow \ldots(A)_x\text{-}(B)_y\text{-}(A)_z\ldots \rightarrow \bullet\bullet\bullet ABBABAABA \bullet\bullet\bullet \quad (5)$$

It has been demonstrated [104] that the rates of the direct and reverse reactions are identical. This is quite understandable, considering that the bonding energies of broken and reformed bonds are almost the same in both directions. Nevertheless, randomization proceeds as a practically irreversible process (under given conditions) and eventually a random copolymer obeying Bernoulli statistic is formed [104].

In the case of ester-ester interchain reactions at elevated temperatures, usually above T_m, the randomization is driven only by the large entropy increase originating from the transition of the block copolymer into a random one. This results in the final randomization of the blend and in a drastic change of its properties - crystallization ability, solubility, transition temperatures, etc.

Performing experiments with blends of crystallizable or non-crystallizable polycondensates, the partners being thermodynamically miscible or non-miscible, it has been unambiguously demonstrated that annealing above the melting temperature results in a complete randomization. At the same time annealing the random copolymer below the melting temperature (some 20°C) leads to the restoration of the blocky structure. Figure 8 demonstrates these two cases for the blend PET/polyarylate (PAr):

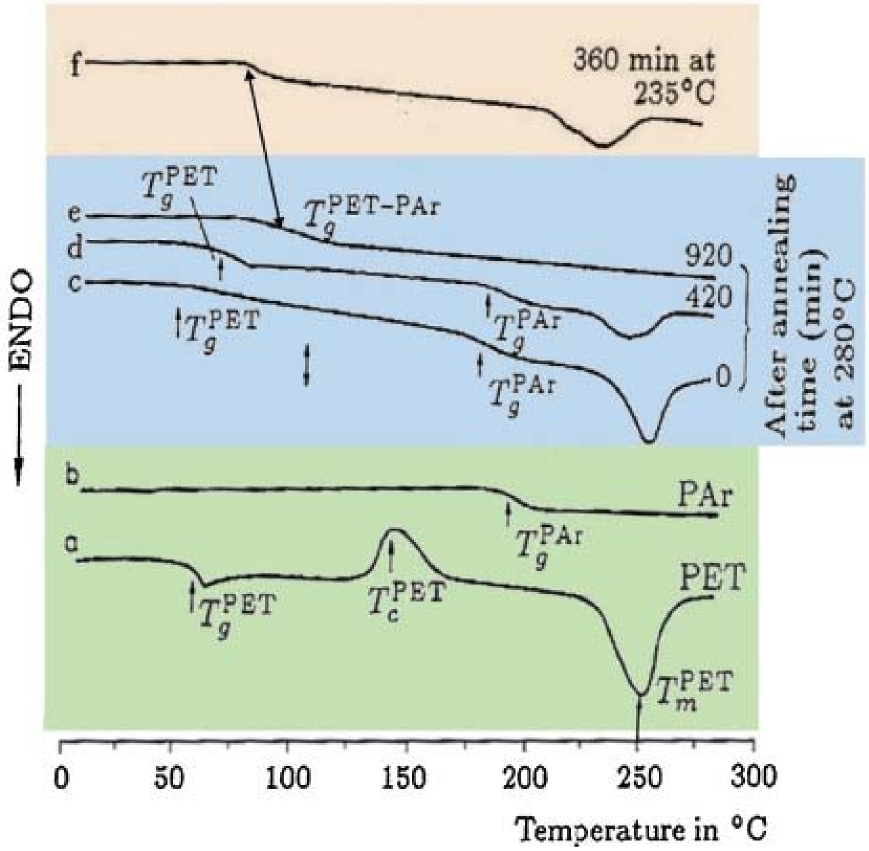


Figure 8: DSC curves of the PET/Par (50/50wt%, or 62/38 molar ratio), taken in heating mode at 10°C/min, after various annealing times at 280°C and 235°C. Sample weight: 7.62 mg. Curves of the starting PET and PAr are given for comparison. Sample weight: 12.0 and 9.0mg, respectively [108]. The color codding is used to illustrate the transition to random (blue) and back to blocky (braunish) state of copolymers; green – the starting homopolymers. Source: Denchev Z., Fakirov S., Sarkissova M., Yilmaz F.: Sequential reordering in condensation copolymers. 2. Melting- and crystallization-induced sequential reordering in miscible poly(butylene terephthalate)/polyarilate blends. Macromolecular Chemistry and Physics, 197, 2869–2888 (1996). Copyright 1996 Wiley-VCH Verlag GmbH & Co. KGaA.

Considering the fundamental statement that transreactions do not determine the type of sequential order and that they are just a tool for its realization, it might be possible to observe such a situation, when other factors appear in the system, acting more strongly than and in opposition to those causing randomization to take place. A good example in this respect is the crystallization. It becomes effective when a randomized condensation copolymer is brought to a temperature below the melting of the crystallizable blend component.

ii. *Crystallization-induced sequential reordering in condensation copolymers*

Figure 9 illustrates schematically the transition from a random into a block copolymer, suggesting that crystallization is the driving force for sequential reordering after cooling a randomized copolymer to a temperature below the T_m of the crystallizable component. It is quite evident that sequences of 2-3 repeating units are not long enough to form a lamella of thickness l_c. The lowest values of l_c are about 50-60 Å, as demonstrated for poly(butylene terephthalate) copolymers [109]. Assuming these values of l_c to be the lower limit and considering that the length of the PET repeat unit in the chain-axis direction is about 11 Å, it is easy to conclude that crystallization of PET can occur only if PET blocks of at least 5-6 repeating units are available. This axiomatic requirement can be considered as the basic driving force toward the blocky structure when crystallization conditions are established [107].

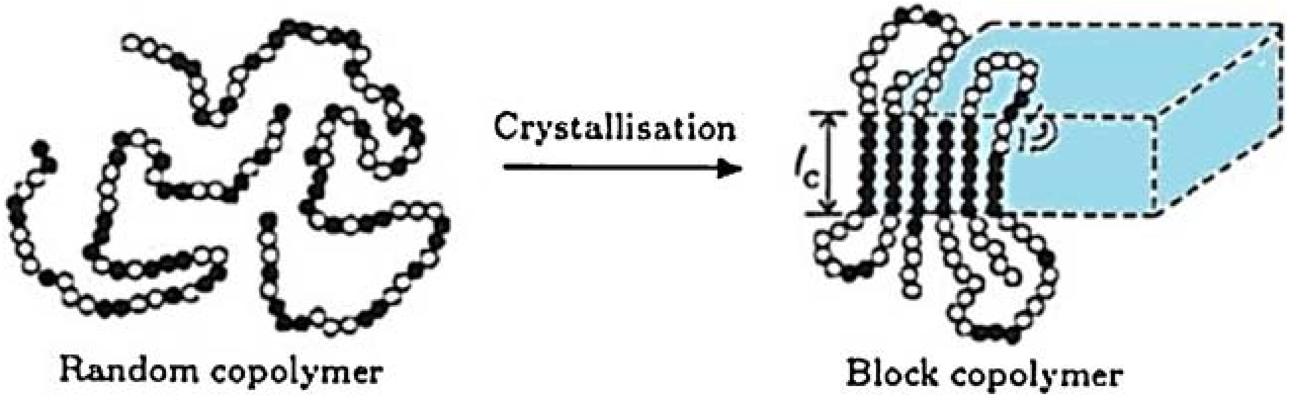


Figure 9: Schematic representation of the transition from random to block copolymer taking place via transreactions under the influence of crystallization [110].Source: Fakirov S., Sarkissova M., Denchev Z.: Sequential reordering in condensation copolymers. 1. Melting- and crystallization-induced sequential reordering in immiscible blends of poly (ethylene terephthalate) with polycarbonate or polyarylate. Macromolecular Chemistry and Physics, 197, 2837-2867 (1996). Copyright 1996 Wiley-VCH Verlag GmbH & Co. KGaA.

The model depicted in Figure 9 demonstrates another important peculiarity of crystallization-induced sequential reordering. Formation of lamellae of thickness l_c not only stimulates sequential reordering in favor of the blocky structure, but also restricts the block length to the value of l_c so one can speak in this case of "microblock copolymers" with quite uniform block length distribution, that is controlled block regeneration.

Crystallization-induced sequential reordering is only one of the possible cases in which the sequential order in condensation copolymers is changed. It was worth looking for copolymer systems where the transition from a random copolymer to a blocky one is governed by factors not related to crystallization.

iii. *Miscibility-induced sequential reordering in condensation copolymers*

One can design an equimolar terpolymer in a two-stage preparation process. Let us have three condensation homopolymers $(A)_n$, $(B)_m$ and $(C)_p$; the first two, $(A)_n$ and $(B)_m$, are immiscible, while $(B)_m$ and $(C)_p$ are miscible. During the first stage of preparation, randomization in the A/B blend takes place:

$$(A)_n + (B)_m \rightarrow \ \ldots ABBBAABBABBAABB\ldots \qquad (AB)_{n=m} \tag{6}$$

After completion of the randomization, the copolymer $(AB)_n$ is melt-blended with the third homopolymer $(C)_p$ and further randomization occurs, resulting in a random terpolymer:

$$(AB)_n + (C)_p \rightarrow \ \ldots AABCCABBACBCC\ldots \qquad (ABC)_{n=m=p} \tag{7}$$

The randomization takes place in the melt via interchain reactions at temperatures above the melting points of all crystallizable components as manifold demonstrated (e.g. [98]). If the randomized terpolymer (eq.(7)) is kept for a longer time in the molten state, one can expect changes in the sequential order in favor of the blocky structure:

$$(ABC)_n \rightarrow \ \ldots AAAAABBBBBCCCCCC\ldots \qquad \ldots(A)_x - (B)_y - (C)_z\ldots \tag{8}$$

This expectation is based on the miscibility of the homopolymers $(B)_m$ and $(C)_p$. Since miscibility requires interaction between longer polymer chains, a tendency toward the formation of longer B- and C-sequences should exist. If one considers that transreactions frequently occur in the melt, the formation of blocks (eq. (8)) seems to be very probable as confirmed experimentally [111]. For this purpose, two systems each one comprising 3 homopolymers have been used. The first one consists of poly(butylene terephthalate)/polycarbonate/polyarylate (PBT/PC/PAr) where PBT and PAr are thermodynamically miscible. The second one involves PBT, PA 66 and PAr, where again PBT and PAr are miscible. In both cases the results obtained confirmed the sequential reordering described schematically by eqs. (6), (7) and (8) [111].

In the above-described cases of sequential reordering in condensation copolymers were discussed the experimental results exclusively from the DSC studies. It should be mentioned that these results and conclusions were supported by parallel studies by means of size exclusion chromatography combined with NMR after selective degradation [112,113]. For some cases it has been used also wide-angle X-ray scattering [110].

In summary, the repeatedly reported randomization of molten condensation block copolymers is observed again and proved by various techniques sensitive to the changes in the crystalline and/or the amorphous phases. The process is accompanied by a loss of crystallization ability. This *melting-induced sequential reordering* is driven mostly by the entropy increase.

Restoration of crystallization ability is observed after annealing of random condensation copolymers and attributed to regeneration of crystallizable blocks. This *crystallization-induced sequential reordering* is driven by upsetting the random ⇄ blockpolymer equilibrium during the annealing of the random system.

Restoration of crystallization ability is also observed in random terpolymers obtained by melting-induced sequential reordering of ternary homopolymer blends, in which two of the constituents are thermodynamically miscible over the entire concentration range. The effect is established by subjecting these terpolymers to prolonged annealing at the same temperature as copolymer preparation. In this *miscibility-induced sequential reordering* the process of block restoration is driven by the miscibility factor.

Both randomization and block regeneration are dependent on temperature, transesterification catalyst, and miscibility of blend components. These processes are composition-sensitive and seem to be related to the specific chemistry of the interchange reactions and starting homopolymer structures. The results obtained show that in the transition from block to random copolymer, (i.e., from longer to shorter blocks), the sample crystallizability decreases, attaining eventually a complete amorphization (as revealed by DSC). Likewise, regeneration of melting endotherms in the crystallization-induced reordering process should reflect the restoration of longer blocks of a crystallizable component. All these changes in the sequential order of condensation copolymers affect drastically their structure and properties [114].

The above definitions describing the three most important cases of sequential reordering in condensation copolymers, including also the factors determining the respective type of order, were formulated in refs. [108,110,111], respectively. They were not only well accepted and widely used but were also proven correct through computer modeling and further experiments (e.g. [115]).

It seems important to stress again that all the analysis related with the sequential reordering in condensation copolymers are based on the understanding that exchange reactions do not determine the type of the sequential order; they represent a tool only for realization of a given type of ordering and this type is determined by other factors in the system.

d) Chemically released diffusion via transreactions

Studying the new phenomenon of *chemical healing* in condensation polymers [86, 87] as result of chemical interactions at elevated temperatures, the concept of "*chemically released diffusion*" was formulated [89] and supported later by Economy et al. [106]. This aspect demonstrates that mass transfer in condensation polymers at temperatures close to the melting point, as well as in the melt, is paralleled by chemical reactions mostly of exchange type shown above. The contribution of the latter to the mass transfer depends strongly on the temperature, reaction conditions (pressure, catalyst, media, etc.), and most likely on the number of favorable contacts between the different chains. It is to be expected that this number will increase with increasing temperature because of chain relaxation.

The results described above allow to make some inferences concerning the diffusion mechanism for long chains in linear condensation polymers at elevated temperatures. It seems quite likely that the transport of sections of macromolecules through the bulk is due not only to physical diffusion processes but also to chemical ones. If the temperature is high enough, a section of macromolecule (a segment or repeating unit as the smallest possible section) does not remain in its original macromolecule. Due to transreactions between different molecules, some sections frequently change their neighbors. Furthermore, the chemical composition of the section itself could be changed if transreactions occur between chemically different molecules.

In such cases, that is, when transreactions are possible (transesterification, transamidation, transetherification, etc.), we can speak of "*chemically released diffusion*" of the macromolecular chains as suggested in [89]. This aspect further demonstrates that mass transfer in this type of polymers at temperatures close to the melting point, as well as in the melt, is accompanied by such chemical reactions. The contribution of the latter to the mass transfer depends strongly on the temperature and reaction conditions (pressure, catalyst, media, etc.). It seems that "chemically released diffusion" will not be sensitive to molecular weight. The determining factor is most likely the number of favorable contacts between the different chains. It is to be expected that this number will increase with increasing temperature because of chain relaxation. As demonstrated by measurements using small-angle neutron scattering, these contacts are quite intensive [97].

The presence of entanglements (stressed points) will favor the exchange reactions, as mentioned above [95]. The higher their concentration, the larger the contribution of chemically released diffusion. The efficiency of the stressed points depends on temperature in the same way as in the case of "neighboring" contact and for the same reason.

The concept of chemically released diffusion was seriously supported by similar experiments with chemically cross-linked polyesters performed by Economy et al. [105,106].

Concluding this subsection, it seems interesting to cite an opinion regarding the chemically released diffusion, expressed in a review article on the recent advances of hierarchical and sequential growth of macromolecular organic structures on surface [116]:

"Before continuing, a distinction should be made between "self-assembly", which is commonly used to evoke the formation of both supramolecular and covalent phases on-surface, and "chemically released diffusion". Indeed, numerous published or being published articles comprise the terminology "self-assembly" whereas the right term is "chemically released diffusion". Indeed, "self-assembly" refers to the self-organization of molecular tectons on surface without necessarily involving a chemical modification of the molecular tectons and this terminology is well-adapted for supramolecular phases for which the cohesion is ensured by weak intermolecular interactions between elemental building blocks. Contrastingly, chemically released diffusion refers to mass transfer occurring in polycondensates due to the permanent exchange of fragments existing between molecular segments under growth (i.e., via transreactions). This concept developed in the early 1980s by Prof. Stoyko Fakirov is more adapted to describe the formation of covalent phases on surface, the chemical composition of the polymer under growth continuously evolving by exchange reactions" [116].

V. KINETICS OF EXCHANGE REACTIONS IN MELTS OF CONDENSATION POLYMERS

The above rather detailed analyses of the occurrence of additional condensation and exchange-(trans) reactions in condensation polymers was done with the only purpose to demonstrate that these reactions not only exist but they play important role in polymer science and technology. Only using these types of reactions, it is possible to manufacture special polymer materials as bottle grade PET, condensation copolymers from polymer blends, realization of the compatibilization phenomenon in polymer blends, etc.

The same reactions, particularly the exchange reactions, offer a new insight on fundamental theoretical properties of polymer systems as for example the diffusion mechanism in melts and solutions of condensation polymers as demonstrated in the foregoing paragraph dealing with the chemically released diffusion. The evaluation of the contribution of exchange reaction in the diffusion process and its mechanism assumes a better knowledge of kinetics of exchange reactions in melts of condensation polymers.

The fundamental development of the kinetics of condensation reactions in polymer chemistry has been done by Carothers [117] and Flory [55] with later contributions of other researchers [98]. Various techniques have been used for studying the additional condensation and exchange reactions as IR spectroscopy (e.g. [104]), NMR spectroscopy (e.g. [118]), WAXS (e.g. [119]), and others. Of particular importance for the purpose of the current review are the studies performed by means of small angle neutron scattering (SANS) on blends of protonated and deuterated species (e.g. [120-122]).

For example, Kugler et al. studied the rate of the interchain transreactions between deuterated and non-deuterated PET chains at 280°C and calculated approximately 10 transesterification reactions occurring per molecule per minute [97]. This means that for fiber grade PET (with a molecular weight of ~ 20 000, i.e. degree of polymerization n ~100) each minute fragments of 10 repeating unit leave a given molecule and join another neighboring one. With increase of the melting temperature the exchange reactions become more intensive and the migrating blocks considerably shorter.

The potential for very rapid transreactions in the copolyesters has been demonstrated by heating a 50/50 mixture of the two homopolymers of poly(acetoxy benzoic acid) and poly(2,6-hydroxynaphtoic acid) at 450°C – the rates are more than 100 ester interchange reactions per chain per second [105]! In addition to the temperature, transreactions are favored by the presence of entanglements, as mentioned above - the higher their concentration the more intensive exchange reactions.

The experiments on chemical healing with cross-linked polyamides [92] and polymers distinguished by extremely high glass transition temperatures [96] demonstrated that the chemically released diffusion is a principal mode for mass transfer in condensation polymers. Further on, the mechanism by which the adhesive bond forms in both liquid crystalline polymers and thermosetting polyesters has been investigated using secondary ion mass spectroscopy (SIMS) and neutron reflection techniques [106]. These complementary analytical techniques have been used to examine the entire range of physical and chemical diffusion distances possible in the aromatic copolyesters. Long range effects could be examined by SIMS while neutron reflection would be able to detect localized interfacial diffusion. The contrast across the interface for the aromatic copolyesters has been achieved by observing the interpenetration between thin films of deuterated and non-deuterated copolyesters.

No observable changes in SIMS depth profile were registered with annealing after 10 h at 280°C. Since the depth resolution of SIMS is 500 Å, any changes on the polymer-polymer interface are predicted to occur over length scales of less than 500 Å. Neutron reflection data suggest that the actual amount of interpenetration is less than 300 Å after 11 h at 280°C [106].

Since the individual films were cured into infinite molecular weight networks prior to joining and annealing, physical diffusion of individual polymer chains or fragments across the interface would not be possible. Thus, the only mechanism available for adhesion across the polymer-polymer interface would be chemical interdiffusion through rapid high-temperature interchain transreactions [106].

VI. ON THE APPLICABILITY OF "REPTATION MODEL" TO MELTS OF CONDENSATION POLYMERS

Coming back to the basic question regarding the diffusion mechanism in melts of non-condensation and condensation polymers at high temperatures, it seems important to try to assess the applicability of the "Reptation model" to melts of condensation polymers. The presented above data on the peculiar only for condensation polymers chemical reactions and their importance for polymer science and technology demonstrate that the classical picture of self-diffusion in polymers, or the "Reptation model", as proposed by de Gennes [2] and Edwards [3], needs to be complemented. Contrasting the non-condensation polymers where the "Reptation model" is the only mechanism for explaining the diffusion process, the case of condensation polymers seems to be more complex. At lower temperatures (for example, up to T_m + 100°C) it looks that the diffusion mechanism is according to the Reptation concept but with some peculiarities - parallel occurring exchange reactions (transesterification, transamidation, transetherification, etc.). If the temperature is high enough, a given fragment no longer appertains to its initial macromolecule. Due to transreactions between different macromolecules, macromolecule's fragments frequently change their immediate neighbors. Furthermore, the chemical composition of such a fragment can change, if transreactions occur between chemically different macromolecules.

This process of continuous leaving from a given macromolecule of fragments, which join another macromolecule (or even the same) is schematically presented in Figure 10.

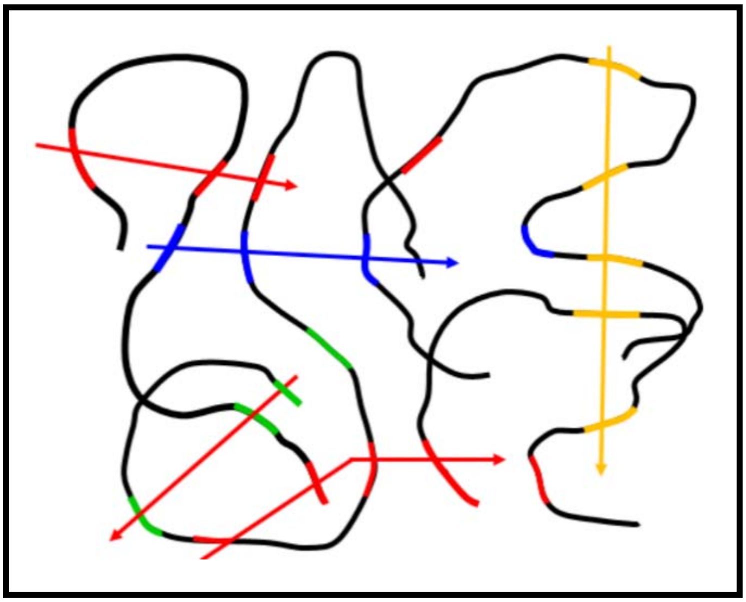


Figure 10: Schematically the diffusion mechanism in melts of condensation polymers – fragments of a given macromolecule are leaving it and are incorporated in a neighbouring second, third, fourth … macromolecule via transreactions. The colour codding demonstrates the fragments and their direction of movement, which is not necessarily according to a straight line. The use of two colours only would realistically reflect the case of a blend of two chemically different condensation polymers.

Completely different is the situation at much higher temperatures. As already mentioned above, in the melt of condensation polymers in each macromolecule, each second takes place breaking the contacts between the neighbouring repeating units. Before establishing a contact (chemical bond) with new (or previous repeating units) the fragment can move, diffuse. However, these fragments move as a single repeating unit (or as small blocks of them) and not as whole long macromolecules. What is more, the macromolecules as long real chains do not exist anymore since the chemical bonds between the repeating units are frequently broken and re-established again (but not necessarily between the previous neighboring repeating units). The macromolecules as stable chains with constant chemical composition appear when the temperature is lowered and the intensity of transreactions is drastically reduced.

In molten blends of condensation homopolymers, one can distinguish two stages of diffusion, due mostly to the different driving force of the mass transfer. During the very first moments of chemical interactions between two homopolycondensates, a block copolycondenste is formed, which further randomize in a random copolycondensate according to eq. (9). The driving force for these changes in the sequential order is the entropy increase during the transitions:

$$\text{Two homopolymers} \rightarrow \text{Block copolymer} \rightarrow \text{Random copolymer} \quad (9)$$

It is also possible to say that the driving force is the concentration gradient leading to a homogeneous distribution of the two chemically different repeating units in the whole volume.

During the second stage, when complete randomization is achieved, the driving force for the mass transfer is the Brownian motion only. The independent kinetic elements, in this case, are the smallest fragments of macromolecules comprising one or a few repeating units. Their motion is schematically illustrated in Figure 11, where the single black particles represent the fragments, which leave a given macromolecule and join another one. This takes place continuously, resulting in mass transfer in an arbitrary direction. This diffusion mechanism is rather a like to that of the low molecular substances and is quite different from the diffusion mechanism illustrated by the “Reptation model”, as recently suggested [123].

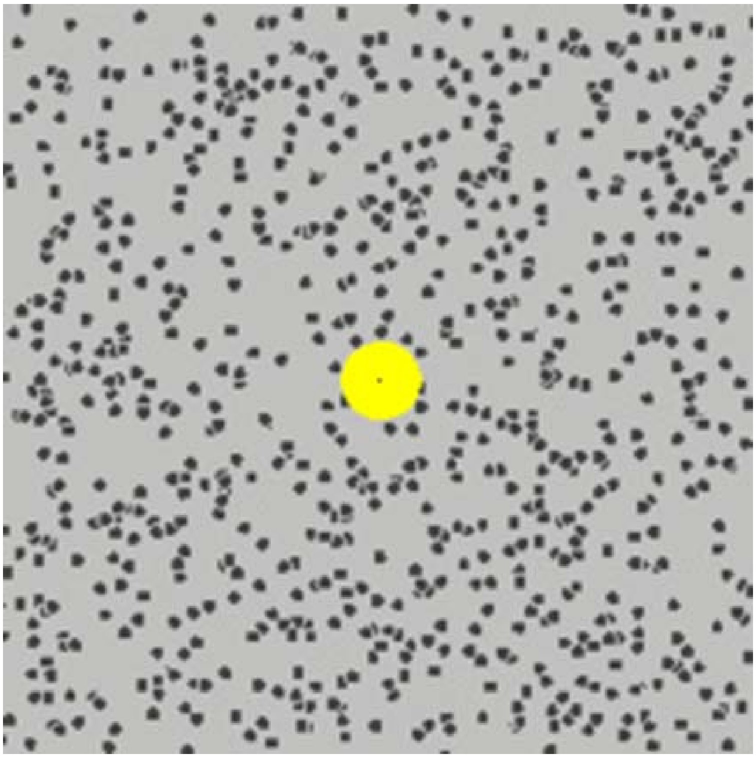


Figure 11: Schematically the diffusion mechanism in melts of condensation polymers at extremely high temperatures (T_m + 100 °C and above). The single independent kinetic elements (black particles) are short fragments of macromolecules, comprising one or a very small number of repeating units, which move in any possible direction. Large, flexible, entangled, and stable formations (macromolecules), to which one could apply the “Reptation model” for explaining the diffusion mechanism, are missing. (The motion can be seen by clicking here).The yellow object represents a particle with much larger sizes.

Slightly different is the situation when one deals with a melt of a single polycondensate. In such cases, the first stage is missing, since practically there is no entropic contribution to the mass transfer and the diffusion is related to the Brownian motion only, as visualized in Figure 11.

Let stress again that the main task of this study is to demonstrate that the diffusion mechanism in melts of condensation polymers above some temperatures could be different from the mechanism offered by the Reptation model, which is based on the concept of segmental motion of macromolecules. Above a given molecular weight (or degree of polymerization) independent kinetic entities are not the macromolecules as a whole formation but their segments. The segments comprise one or a few repeating units (in a case of flexible molecules) or the whole macromolecule (in a case of rigid molecules as those of liquid crystalline polymers) and allow us to describe the behavior of polymers by means of the lows derived for the low molecular weight substances[5].

This means that for the describing the kinetic properties of macromolecules (deformations, diffusion, mass transfer, etc.) we are using not the whole molecules but their segments, i.e. much shorter formations than the whole molecules. This approach, namely considering the macromolecules as comprised of many kinetically independent elements for describing many polymer properties is applicable to all polymers, the non-condensation and condensation ones. The same approach is a basic element of the "Reptation model" – movement in a snake-like way.

At the same time, as already discussed, an inherent property of condensation polymers is their ability to undergo intensive interchange (trans) reactions in their melts above some temperatures. This means further dissipation of macromolecules to shorter sections. The situation is like the case of "decomposition" of macromolecules to segments, but there is a substantial difference between the two cases. While segments do not exist as real independent formations, the sections comprising one or a few of repeating units really exist. They not only exist but they move in a rather freeway in the melt as independent kinetic elements. Since their sizes are in range of the sizes of the common non-polymeric molecules, their diffusion mechanism must be close to that of low molecular weight substances and different from the diffusion mechanism of macromolecules suggested by the Reptation concept.

The fact that the macromolecules of condensation type do not exist anymore at higher melt temperature as whole entities, but as truly short sections is well established and accepted. For some unknown reasons, this fact is not considered by the specialists researching the diffusion and mass transfer processes in melts of condensation polymers. Possibly because all studies related with the Reptation concept have been performed with non-condensation polymers, as also demonstrated by a recent review on modeling of entangled polymer diffusion in melts and nanocomposites [124].

VII. CONCLUDING REMARKS

Summarizing the above considerations, we could conclude that the diffusion mechanism in polymer melts could be at least of two types. Depending on molecular weight and temperature, or more precisely, dealing with substances with relatively low molecular weights (monomers, oligomers, that is before reaching the molecular weight of the segment) independent kinetic elements are the whole molecules and the diffusion mechanism is the same as that in the melts of low molecular weight substances.

With the further rise of the molecular weight, i. e. above that of the segment, the independent kinetic elements are the segments. Their number in a single macromolecule depends on its flexibility – the higher the flexibility the shorter the segment length and the larger their number is [5]. The diffusion mechanism is segmental to which could be applied the Reptation concept.

Dealing with melts of condensation polymers it should be noted that the outlined two diffusion mechanisms are valid for melt temperatures not much higher than the melting temperatures. With further rise of melt temperature (for example, for PET it is above (T_m + 100°C) very intensive exchange reactions take place, which results in a drastic change of the diffusion mechanism – the independent kinetic elements are not the molecules neither the segments but the repeating units or their small blocks with sizes typical for the molecules of low molecular weight substances. It follows that the diffusion mechanism for this range of temperatures is the same as that for the case of the melts of low molecular weight substances.

In conclusion, the diffusion mechanism in polymer melts could be of two types – molecular and segmental. The Reptation concept can be applied to segmental type of diffusion only. It follows that for melts of condensation polymers at extremely high melt temperatures the "Reptation model" cannot be used for explanation of the diffusion mechanism since independent kinetic elements are the repeating units, that is the mechanism is molecular.

In Figure 12 an attempt is undertaken to present schematically the described situation stressing on the individual kinetic elements and the respective diffusion mechanism in melts.

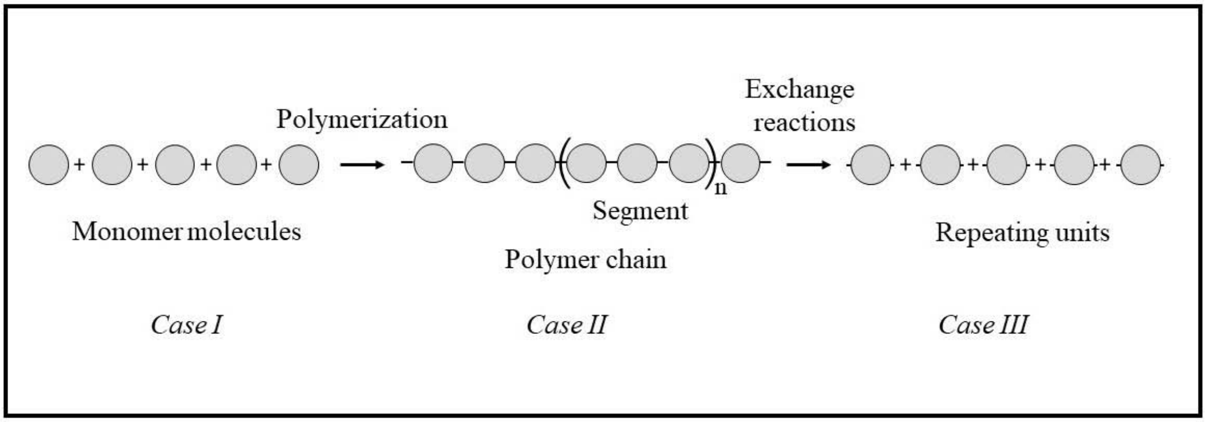


Figure 12: Schematically the formation of polymer chains (Case II) from monomer molecules (Case I) and dissipation of chains into chemically non-bonded repeating units (Case III): ○ - monomer molecules, -○-○-○- - polymer chain comprised of chemically bonded segments, -○- - repeating unit. Diffusion mechanism: Case I - "jump-like" (Frenkel), Case II – "snake-like" (de Gennes), Case III: - as Case I.

Finally, it seems important to mention that the phenomenon taking place in the melts of condensation polymers at extremely high temperatures was analyzed 40 years ago and called "*chemically released diffusion*" [89]. Some later this approach was supported by Economy et al. [106]. Very recently [53], it was discussed again in relation to chemical peculiarities of condensation polymers, as well as commented by Pigot and Dumur [116] in their review on recent advances of hierarchical and sequential growth of macromolecular organic structures on surface. They state that the concept of chemically released diffusion is more adapted than "self-assembly" to describe the formation of covalent phases on surface, the chemical composition of the polymer under growth continuously evolving by exchange reactions [116].

The dissipation of macromolecules into single repeating units because of proceeding of exchange (trans) reactions in the melts of condensation polymers is well-known and many-fold documented fact [53-55, 68,69,86,87,89-92,96-98,103-108,110-115,118-122]. Nevertheless, it remains neglected by the researchers studying various processes in polymer melts (flow, diffusion, mass transfer, deformation, and others) as well as their mechanisms. A good example in this respect is the fact that studies on reptation mechanism have been performed exclusively on non-condensation polymers (e.g. [17-20]).

The role of the independent kinetic entities in melts can be played by the single (small) molecules, by the segments (in case of macromolecules), and by the chemically non-bonded repeating units (in case of condensation polymers at the highest possible temperatures) as schematically shown in Figure 12. The "Reptation model" can be used for explanation of diffusion mechanism only in cases of segmental type of motion. This means that the Reptation concept is not applicable to melts of condensation polymers at highest possible temperatures where the diffusion is realized by the single chemically non-bonded repeating units.

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