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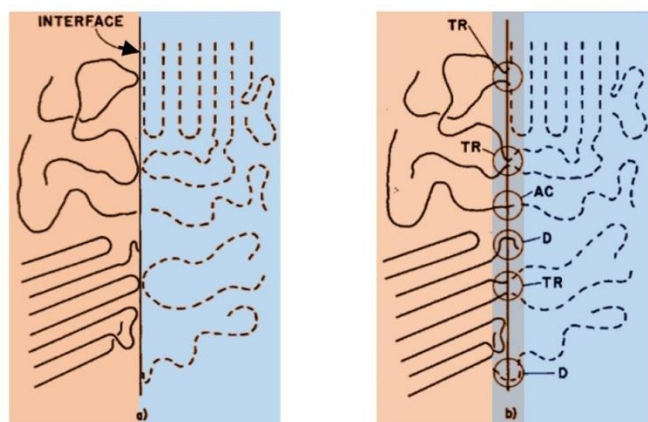
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## Condensation Polymers: Their Chemical Peculiarities Offer Great Opportunities

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### Graphical abstract



Chemical healing process in a semicrystalline linear polycondensate at temperature close (but below) to the melting: (TR) transreaction, (AC) additional condensation, (D) diffusion

### Abstract

This review represents an attempt to describe and to discuss a couple of phenomena arising from the unique ability of condensation polymers to undergo post chemical interactions – additional condensation and trans- (exchange-) reactions, contrasting the rest of polymers. To them belongs the chemical healing – self-repairing of damaged polymer materials and articles via additional condensation and transreactions, which, together with the physical healing, i.e. a healing due to physical diffusion of macromolecules, are considered as the only cases of a real self-healing.

Another result is the phenomenon of chemically released diffusion, the case when the mass transfer is paralleled and made possible mostly due to the exchange reactions. In this case, parts of a macromolecule leave it and are incorporated in another molecule thus making the chemical composition of macromolecules continuously changeable, particularly in polymer melts.

The third phenomenon related with the specific for condensation polymers chemical interactions is the well-known and widely studied sequential reordering in condensation copolymers. Clear definitions of the basic cases including the factors determining the respective

type of order are discussed. Their analysis is based on the understanding that other factors in the system determine the sequential order – the additional condensation and transreactions are a tool only for realization of one or other sequential order in condensation copolymers but by no means have they determined it.

The review stresses on the fundamental importance of these reactions for polymer technology, particularly of the additional polycondensation. Large branches of polymer industry (including also recycling) are based on this process related to the increase of molecular weight of the primary synthesized polyesters and polyamides.

The main target of the review is to demonstrate that these often-overlooked chemical reactions could be helpful even today in our attempts to create new or improve the existing polymer materials.

**Keywords:** Additional condensation, Trans- (exchange-) reactions, Chemical healing, Chemically released diffusion; Corresponding author: <s.fakirov@auckland.ac.nz>

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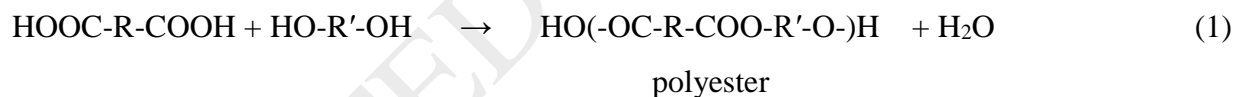
## 1. Introduction

Let us not forget a very basic knowledge. Polymers are synthesized mostly by two chemical reactions - the polycondensation and polymerization. In the first case the functional groups (e.g. -COOH, -OH, -NH<sub>2</sub>, and others) of the monomers react and a low molecular weight product (usually H<sub>2</sub>O) 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:*



*Polymerization:*



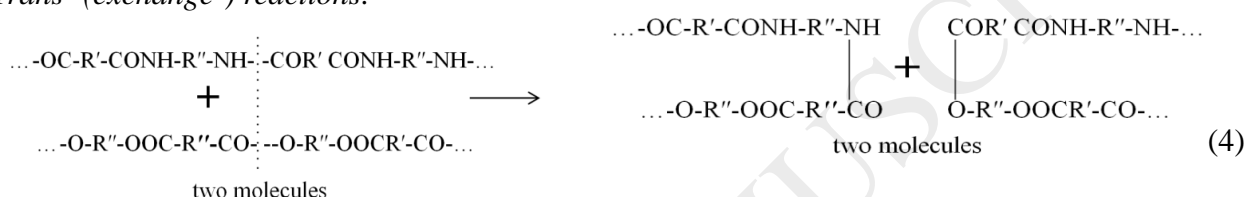
Some polymers, regardless of their type of synthesis, contain as side groups various functional groups (-OH, -NH<sub>2</sub>, -COOH and others), which can undergo chemical reactions with similar groups of another polymer if the respective reaction conditions (heat, catalyst, vacuum, etc.) are present. These reactions have the specificity that they do not involve the backbone of macromolecules but their side groups only [1].

The condensation polymers, in addition to this type of reactions, can realize also chemical interactions with the participation of backbone atoms [2,3]. The most typical are the *trans- (exchange-) reactions* and the *additional polycondensation*:

*Additional polycondensation*:



*Trans- (exchange-) reactions*:



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 [1-3]. 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 [3-8] particularly for poly(ethylene terephthalate) (e.g. [9]). 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.

The term “solid-state polycondensation” simply says that chain growth by condensation steps occur where at least one reaction partner exists in the solid state. In fact, the solid-state polycondensation encompasses a broad variety of condensation reactions and substrates [8].

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 [10] that ester interchange reactions of poly(ethylene terephthalate) (PET) 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 [10].

## **2. Commercial importance of the additional (post) polycondensation**

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 to 3 decades PET found a very 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 [11].

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 the 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 discussed above. On the commercial importance of these reactions firstly stressed Flory

in the mid-thirties of last century [3] and later described in the open (e.g. [12]) 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% [13].

### 3. Chemical healing

Self-healing is a well-known phenomenon in nature. For example, a broken bone merges after some time and if skin is damaged, the wound will stop bleeding and heals again. This concept can be mimicked to create polymeric materials with the ability to regenerate after they have suffered degradation or wear. Already are realized applications in aerospace engineering, and current research in this fascinating field shows how different self-healing mechanisms proven successful by nature can be adapted to produce even more versatile materials [14,15].

The concept of “self-healing” of synthetic materials emerged a couple of decades ago and continues to attract scientific community progressively [16-25]. 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 [15,16].

In a recent [26] detailed review on 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*” [26]. 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 very 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 autohesion (direct bonding or self-bonding) and adhesion of polymers [27] undertaken by Voyutskii [28], 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 [27,29-31]. To the same period belongs the formulation of the fundamental concept of “reptation model”, done mostly by De Gennes [32] and Edwards [33]. Their idea was immediately implemented in the molecular interpretation of the healing process [26,27,29]. 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. 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 [26,29].

The self-diffusion in a bulk polymer helps to understand the healing process in the best way, but, the two processes are not identical [29]. 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 [29]. Configurational relaxation in the bulk polymer is usually described by the “reptation model” [32, 33].

It is worth noting that in the crack healing process the following five stages were distinguished: (i) surface rearrangement, (ii) surface approach, (iii) wetting, (iv) diffusion, and (v) randomization [26,29]. By the end of the wetting stage, the chains are free to move across the interface during the following stages of diffusion and randomization, which are the most important ones, because just in these stages the characteristic strength of a polymer material appears. Interesting enough, these two stages are also the most time consuming in the whole healing process [29].



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 [34].

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 [34].

Supporting this assumption is the observation mentioned above [10] that ester interchange reactions of poly(ethylene terephthalate) take place 20-30°C below  $T_m$ , e.g., 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 [34]. Two such strips are partially overlapped as shown in Fig. 1, pressed, and heated in a vacuum at 240°C for 10 to 100 h. By measuring the stress at break,  $\sigma_b$ , outside the contact area and the debonding shear stress,  $\tau_i$ , the critical overlapping length,  $l$ , has been computed. Further experiments [35] lead to the conclusion that transreactions contribute more than solid-state post condensation to the chemical healing.

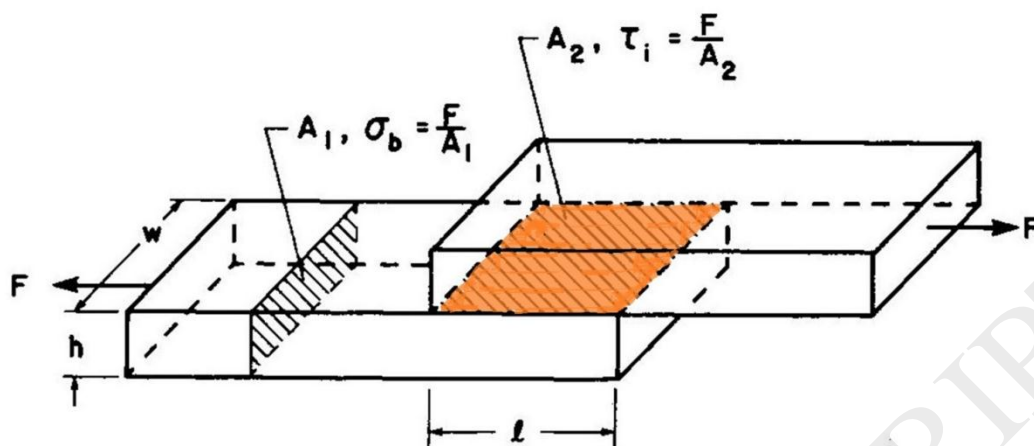


Fig. 1. Schematic geometry of samples used for chemical healing experiments:  $\sigma_b$  – tensile strength,  $\tau_i$  – shear strength. [34]. *Source:* Fakirov S. Chemical healing in poly(ethylene terephthalate). J Polym Sci Polym Phys Ed 1984;22:2095–2104. Copyright 1984 John Wiley & Sons, Inc.

If we apply the above considerations [26,29] to the case in which two linear condensation specimens are undergoing stage iii (wetting) 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). 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 Fig. 2. The diffusion (e.g., mutual interpenetration of the chains) is considered only in amorphous regions (Fig. 2), which for PET represent less than 50% of the surface [34].

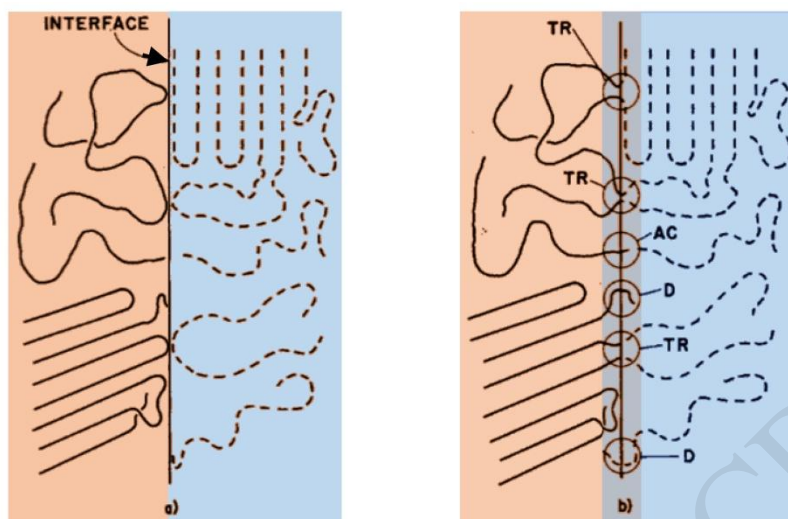


Fig. 2. Schematic of chemical healing process in a semicrystalline linear polycondensate at temperature close (but below) to the melting: (TR) transreaction, (AC) additional condensation, (D) diffusion. [34]. *Source*: Fakirov S. Chemical healing in poly(ethylene terephthalate). J Polym Sci Polym Phys Ed 1984;22:2095–2104. Copyright 1984 John Wiley & Sons, Inc.

Summarizing, it 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 [34] 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 [36] has acknowledged this fact in his review on compatibility and transesterification in binary polymer blends as well as in the recent monograph of H. Kricheldorf [2] 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 polycondensates 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 [37]) to offer self-repairing through the cleavage and reformation of specific bonds [26] 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 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”.

For the cases of chemically assisted healing the responsible for the self-repairing entities are incorporated into polymer networks and are typically categorized into reversible covalent and non-covalent bonds. The presence of these reversible bonds introduces molecular level heterogeneities along a polymer backbone, or as pendent groups, which may further facilitate the formation of new phases with extended length scales [26]. It seems important to stress again that in the above described cases of physical and chemical healing such “*molecular level heterogeneities along a polymer backbone*” [26] are missing and for this reason they should be considered as cases of genuine *self-healing*.

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* [34,35] since it has been demonstrated [38] 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 [38].

All the above described experiments on chemical healing [34,35,38] 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 [39]. 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 [39] 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 lead to the healing experiments with a liquid crystalline polymer [40].

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) [41]. Strips with higher melting temperatures were 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., [42] based on methoxy methylation.

After such pretreatment of the samples the healing procedure is performed with partially overlapped strips (Fig. 1) 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 polycondensates 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 effects 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 [41].

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 [43]. In such a situation, the transreaction processes are favored, and it can thus be concluded that the healing effect is mainly a result of transreactions [41].

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,  $T_g$  [44]. For example,  $T_g$  of Upilex-R (polyimide) is 285°C, and that of Kepton-H (polypiomellitimide) – 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 [44].

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 [44].

#### **4. Chemically released diffusion via transreactions**

The results described above suggests 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 this way, the classical picture of self-diffusion in bulk polymers or the reptation model, proposed by de Gennes [32] and Edwards [33], will become complete only when effects of transreactions in linear polycondensates are also considered. In such cases, that is, when transreactions are possible (transesterification, transamidation, transesterification, etc.), we can speak of “*chemically released diffusion*” of the macromolecular chains as suggested in [38]. 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 (SANS), these contacts are quite intensive [45]. 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 [45]. The potential for very rapid transreactions in the copolyesters has been demonstrated by heating a 50/50 mixture of the two homopolymers of poly(acetoxybenzoic acid) and poly(2,6-hydroxynaphtoic acid) at 450°C – the rates are more than 100 ester interchange reactions per chain per second [46]!

The presence of entanglements (stressed points) will act in the same direction [43]. 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 experiments with cross-linked polyamides [41] demonstrate that the chemically released diffusion is a principal mode for mass transfer in condensation polymers. The concept of chemically released diffusion was further supported by similar experiments with chemically cross-linked polyesters performed by Economy et al. [47].

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 [47]. These complementary analytical techniques were used to examine the entire range of physical and chemical diffusion distances possible in the aromatic copolyesters. The contrast across the interface for the aromatic copolyesters was achieved by observing the interpenetration between thin films of deuterated and non-deuterated copolyesters. 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 (Fig. 2) would be chemical interdiffusion through rapid high-temperature interchain transreactions.

## **5. Sequential reordering in condensation copolymers via transreactions**

The study of transreactions started with the pioneer work of Flory [3]. 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 [10]) resulting in formation of a block copolymer [45]. In the subsequent years they have been widely used for preparation of condensation copolymers starting from blends of homopolymers (e.g. [48]). 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.

Evidence derived from the behavior of the crystalline phases has been demonstrated on melt-blended PET with polyamide 6 (PA 6), where the blend being drawn after extrusion and annealed for various times around the melting temperatures of the blend components [49]. Wide-angle X-ray scattering (WAXS), Fig. 3, demonstrates that the thermal treatment at 220°C for 5 h (Fig. 3a) results in a crystalline highly oriented polymer blend. The situation changes drastically after annealing at 240°C for 5 h (Fig. 3b) - 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 (Fig. 3c).

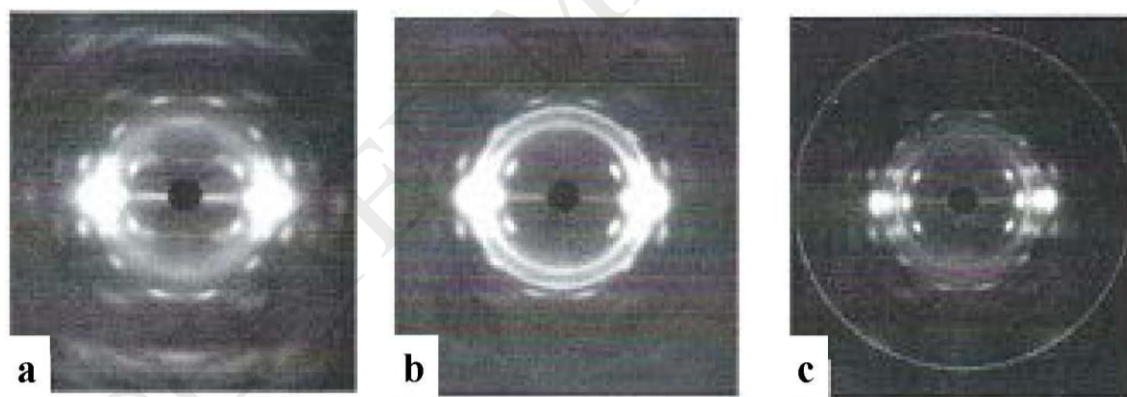


Fig. 3. WAXS transmission patterns of PET/PA 6 blend, zone-drawn and annealed at different temperatures and for various durations: (a)  $T_a = 220^\circ\text{C}$ ,  $t_a = 5$  h, (b)  $T_a = 240^\circ\text{C}$ ,  $t_a = 5$  h, (c)  $T_a = 240^\circ\text{C}$ ,  $t_a = 25$  h. The patterns are taken at room temperature after the respective annealing.

To the same conclusions leads the testing of the same samples by means of differential scanning calorimeter (DSC) as can be concluded from the respective curves displayed in Fig. 4.

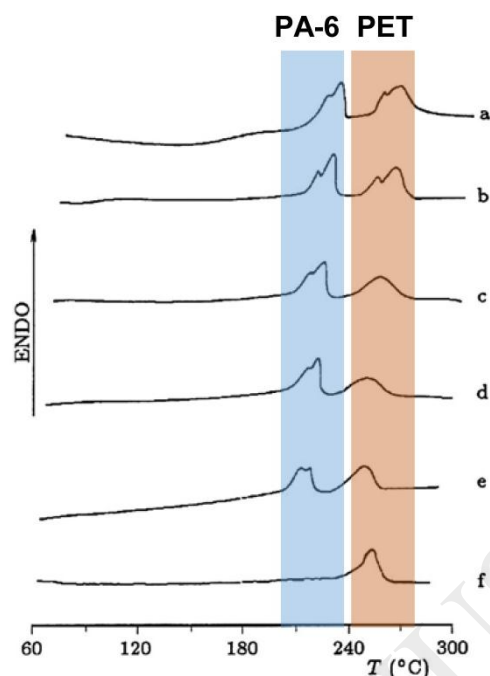


Fig. 4. DSC curves of PET/PA 6 blend (ultraquenched, zone-drawn and additionally annealed at different temperatures and for various durations) taken in second heating mode. Annealing temperatures  $T_a$  and durations  $t_a$ : (a) unannealed, undrawn; (b) unannealed, drawn 4x, (c)  $T_a = 220^{\circ}\text{C}$ ,  $t_a = 5$  h, (d)  $T_a = 220^{\circ}\text{C}$ ,  $t_a = 25$  h, (e)  $T_a = 240^{\circ}\text{C}$ ,  $t_a = 5$  h, (f)  $T_a = 240^{\circ}\text{C}$ ,  $t_a = 25$  h [49].  
*Source:* Fakirov S, Evstatiev M, Schultz JM. Microfibrillar reinforced composite from drawn poly (ethylene terephthalate)/nylon-6 blend. *Polymer* 1993;34:4669-4679. Copyright 1993 Elsevier.

As already mentioned, evidences derived from the behavior of the amorphous phases - the presence and number of glass transition temperatures have been also used for studying the sequential order in condensation copolymers. The same PET/PA 6 blend subjected to drawing and annealing has been used [50]. Again, annealing at lower temperatures, or at higher ones ( $240^{\circ}\text{C}$ ) but for shorter times, leads to the formation of two well-defined and spatially separated amorphous phases, giving rise to two glass transition temperatures,  $T_g^{\text{PET}}$  and  $T_g^{\text{PA6}}$ , for the PET and PA 6 amorphous phases, respectively. Annealing at  $240^{\circ}\text{C}$  for 5 h results in a decrease in the PA 6 amorphous fraction. After annealing for 25 h it disappears completely [50].

This observation indicates 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 (Figs. 3

and 4) and amorphous [50] 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.

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. [51], Deavaux et al. (e.g. [52]), Economy et al. [46,47] 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. [53]). These studies 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. [53]) it has been judged exclusively from the crystallization ( $T_m$ ) and glass transition ( $T_g$ ) behaviors.

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:



It has been demonstrated [52] that the rates of the direct and reverse reaction 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 [52]. To explain this effect, one should bear in mind the well-known relation between the equilibrium constant,  $K$ , and the changes in both, the reaction heat,  $\Delta H$ , and the reaction entropy,  $\Delta S$ :

$$RT \ln K = \Delta H - T\Delta S \quad (6)$$

In the case of ester-ester interchain reactions at elevated temperatures, usually above  $T_m$ ,  $\Delta H = 0$  and 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. Fig. 5 demonstrates these two cases for the blend PET/polyarylate (PAr):

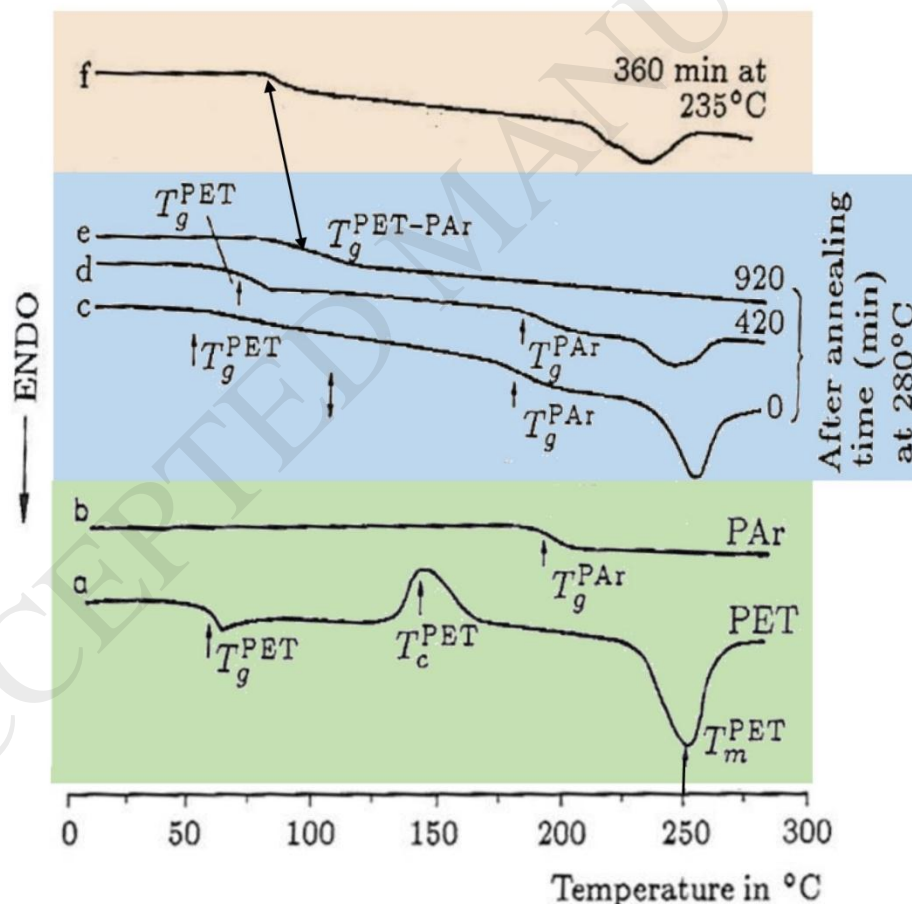


Fig. 5. DSC curves of an equimolar PET/PAr blend, taken in heating mode at 10°C/min, after various annealing times at 280°C and 235°C [54]. *Source:* Fakirov S, Sarkissova M, Denchev Z.

Sequential reordering in condensation copolymers. 1. Melting- and crystallization-induced sequential reordering in immiscible blends of poly(ethylene terephthalate) with polycarbonate or polyarylate. *Macromol Chem Phys* 1996;197:2837-2867. 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.

Reorganization of a random copolymer into a block one has been observed earlier [51] with a sample containing 78.8 ethylene terephthalate units and 21.2 ethylene 2-methylsuccinate units. After a 30 h annealing at 220°C, this sample displayed a small increase of the number-average sequence length of the terephthalate blocks (from 5.3 to 6.8), a two-fold crystallinity increase and a 9°C rise in the melting point. However, as emphasized by Muehlenbach et al. [46], such results concerning crystallization-induced polymerization should be interpreted with caution. Blend compositions close to 80/20 by mol (referred to as repeat units) in favor of the crystallizable polymer, applied in the above studies [51], could have limited the randomization to sequences of 5-6 repeat units, thus affecting the reliability of the conclusions about crystallization-induced reordering. The assumption in [46] has been later [54] proved on the system PET/polycarbonate (PC) demonstrating that the blend PET/PC = 85/15 (mol) cannot be randomized at all.

Fig. 6 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 repeat 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) (PBT) copolymers [55]. 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 [53].

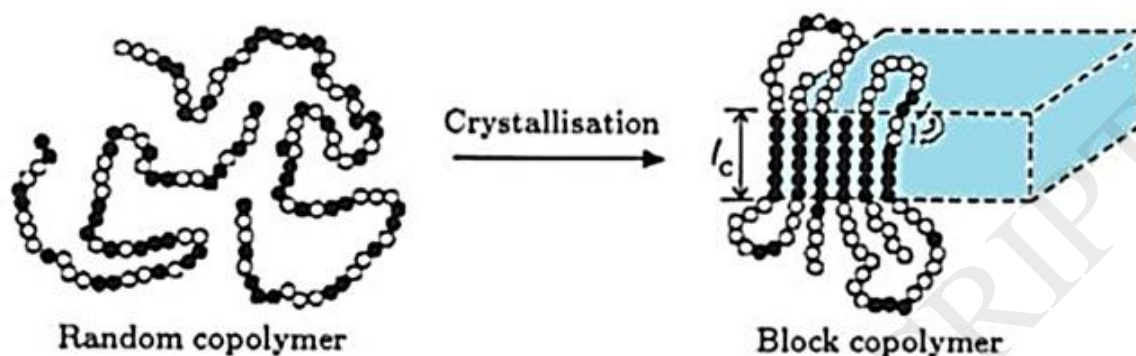


Fig. 6. Schematic representation of the transition from random to block copolymer taking place via transreactions under the influence of crystallization [54], *Source*: Fakirov S, Sarkissova M, Denchev Z. Sequential reordering in condensation copolymers. 1. Melting- and crystallization-induced sequential reordering in immiscible blends of poly(ethylene terephthalate) with polycarbonate or polyarylate. *Macromol Chem Phys* 1996;197:2837-2867. Copyright 1996 Wiley-VCH Verlag GmbH & Co. KGaA.

The model depicted in Fig. 6 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.

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.

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:



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:



This randomization takes place in the melt via interchain reactions at temperatures above the melting points of all crystallizable components as manifold demonstrated (e.g. [48]). If the randomized terpolymer (eq. (8)) is kept for a longer time in the molten state, one can expect changes in the sequential order in favor of the blocky structure:



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. (9)) seems to be very probable.

Similarly, to the above described cases of melt- and crystallization induced sequential reordering [54,56] the conclusions about sequential order are based exclusively on DSC data, assuming that sample amorphization and observation of a single  $T_g$  are results of randomization, and that regeneration of the crystallization ability is due to the restoration of blocks.

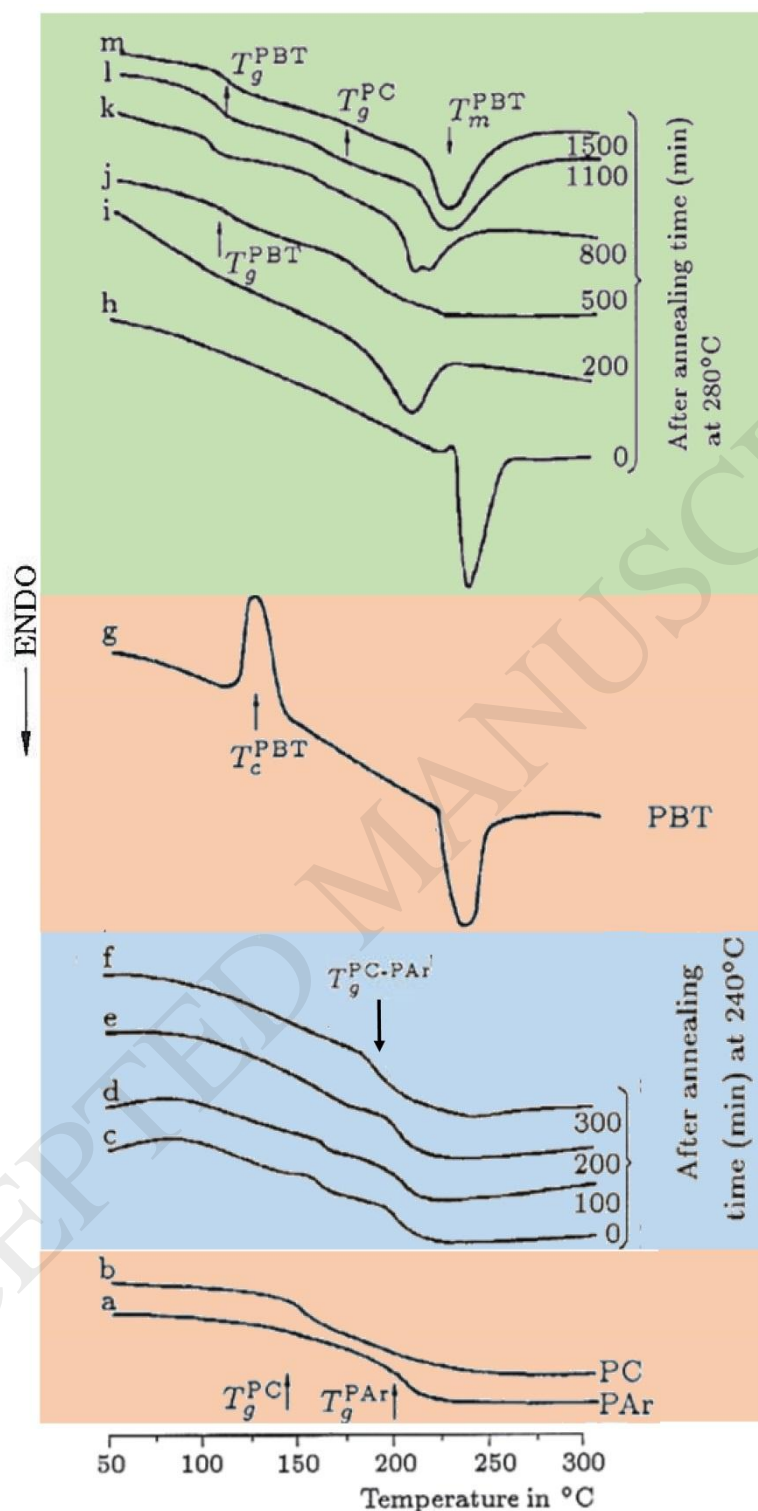


Fig. 7. DSC curves of the PBT/PC/PAr blend, taken in heating mode at 10°C/min, after various annealing times at 240°C and 280°C. Sample weight: 45 mg. Curves of the starting neat PBT, PC, and PAr are given for comparison [57]. *Source:* Fakirov S, Sarkissova M, Denchev Z. Sequential reordering in condensation copolymers. 3. Miscibility-induced sequential



reordering in random copolyesteramides. *Macromol Chem Phys* 1996;197:2889-2907. Copyright 1996 Wiley-VCH Verlag GmbH & Co. KGaA.

DSC curves for the blend poly(butylene terephthalate)/polycarbonate/polyarylate (PBT/PC/PAr) are shown in Fig. 7. The two non-crystallizable homopolymers PC and PAr are solution-blended and the solvent is removed. The blend is then kept for various times at 240°C, a temperature well above the  $T_g$  of both components (Fig. 7c-f). After each annealing time the sample is cooled down to room temperature and the DSC curve is taken by scanning to 280°C. This cycle is repeated until evidence appears for sample randomization, i. e., the two separate glass transitions  $T_g^{PC}$  and  $T_g^{PAr}$  in curve (c) of the unannealed PC/PAr blend merge into a single  $T_g^{PC-PAr}$  in curve (f) of the same sample after 300 min at 240°C. It is a widespread practice to consider such a behavior of the  $T_g$  as an indication of formation of a block copolymer which transforms into a random one when a single  $T_g$  is observed due to transreactions [36,53].

At this stage (after annealing for 5 h at 240°C) the sample is removed from the DSC pan and solvent-mixed with PBT to obtain an equimolar blend of PBT/PC/PAr in which PC and PAr are involved in a copolymer. Without any thermal treatment, the first heating run reveals a strong melting peak of PBT (Fig. 7h) quite similar in its area and temperature position to that of neat PBT (Fig. 7g). This indicates that one is dealing with a physical blend of neat PBT and PC/PAr random copolymer. After application of the same thermal treatment cycle as with the former blend of PC/PAr, but at 280°C, one observes an interesting result: at shorter annealing times (up to 500 min) an almost complete amorphization of the PBT-PC-PAr terpolymer occurs, as can be concluded from the disappearance of the PBT melting peak (Fig. 7j) [53].

Prolonged annealing between 800 and 1500 min at the same temperature results in the recovery of the crystallization ability (Fig. 7k-m). Since the sequential reordering in this case takes place in the melt (280°C) the driving force cannot be the crystallization. The driving force is related to the tendency of PBT and PAr to mix, since it is known [36] that they are miscible in any composition.

The experiments performed with the binary PC/PAr and ternary PBT/PC/PAr blends have been repeated with a similar system comprising PBT, PA 66 and PAr. The only difference is that

the experiments were started with a crystallizable PBT/PA 66 blend. Further behavior of this system is quite like that of the previous system (Fig. 7).

These results lead to the conclusion that after randomization of the terpolymer comprising PBT, PA 66, and PAr by short annealing at 290°C, further annealing at the same temperature results in regeneration of the blocky structure of the copolymer. Again, as in the previous case, the transition of the random copolymer into a blocky one cannot be driven by crystallization factors, since it takes place at temperatures far above the melting of the crystallizable components. Having in mind that the two starting binary blends (PC/PAr and PBT/PA 66) consist of immiscible constituents and only the third component is miscible with one of the first two, it may be assumed that it is the miscibility that accounts for the observed regeneration of the blocky structure. In other words, one can speak about *miscibility-induced sequential reordering in condensation copolymers* [53,57].

The concept of miscibility-induced sequential reordering is visualized in the schematic models displayed in Figs. 8 and 9. The first one illustrates the case when the random copolymer obtained from two immiscible condensation homopolymers,  $(A)_n$  and  $(B)_m$ , is blended with the condensation homopolymer  $(C)_p$ . The components  $(C)_p$  and  $(B)_m$  are miscible. When this blend is annealed at elevated temperatures in the melt, the  $(C)_p$  component reacts with the copolymer and the initial block terpolymer transforms into a random terpolymer (Fig. 8b).

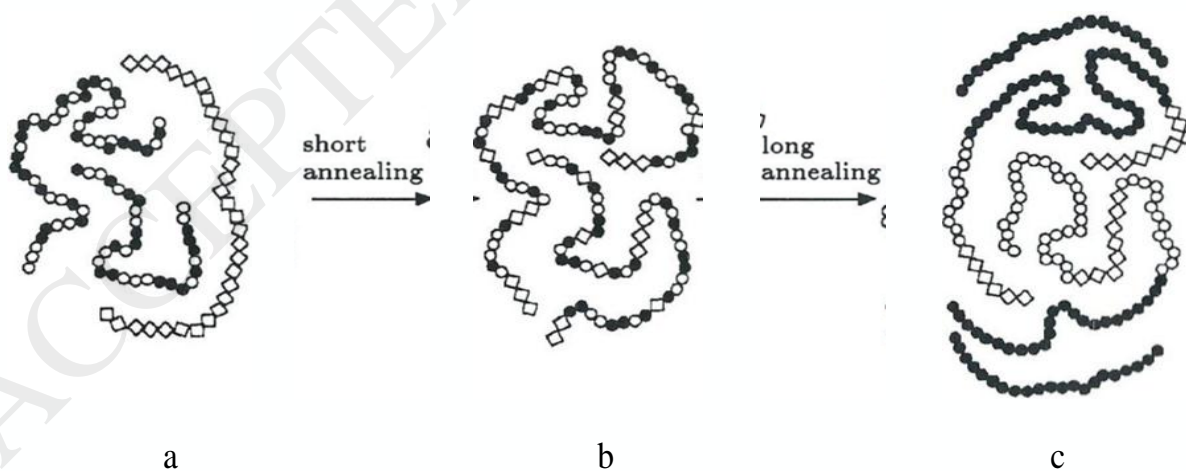


Fig. 8. Schematic representation of the miscibility-induced changes in the sequential order of a terpolymer taking place via transreactions during shorter and longer annealing. The condensation homopolymers are:  $(A)_n$  ( $\bullet$ ),  $(B)_m$  ( $\circ$ ) and  $(C)_p$  ( $\diamond$ );  $(A)_n$  and  $(B)_m$  are

immiscible and non-crystallizable,  $(C)_p$  is crystallizable and miscible with  $(B)_m$  [57]. *Source:* Fakirov S, Sarkissova M, Denchev Z. Sequential reordering in condensation copolymers. 3. Miscibility-induced sequential reordering in random copolyesteramides. *Macromol Chem Phys* 1996;197:2889-2907. Copyright 1996 Wiley-VCH Verlag GmbH & Co. KGaA.

When the random terpolymer  $(ABC)_n$  (Fig. 8b) is kept for a longer time at the same temperature, due to the tendency of  $(B)_m$  and  $(C)_p$  to mix, transreactions in the "opposite" direction take place, resulting in formation of a blocky structure (see eq. (8) or (9)). Dephasing should also take place with the appearance of two phases, the first comprising the  $(A)_n$  component and the second one the  $(B)_m$  and  $(C)_p$  blocks, as shown in Fig. 8c. As a result, the random terpolymer  $(ABC)_n$  is converted into block terpolymer  $\cdots (A)_x - (B)_y - (C)_z \cdots$  [53].

Let us now suppose that one of the components, e.g.,  $(C)_p$ , is crystallizable and the other two,  $(A)_n$  and  $(B)_m$  - non-crystallizable. On cooling of the molten terpolymer below  $T_m$  (Fig. 9a), crystallization should take place (as shown schematically in Fig. 9b) if a blocky structure is available. As a result, one may expect evidence of: (i) the crystalline phase of the  $(C)_p$  component (with its  $T_m^C$ ); (ii) the amorphous phase of the same component (with its  $T_g^C$ ) that is not completely mixed with the amorphous phase of  $(B)_m$ , which should display its  $T_g^B$  too, and (iii) the  $(A)_n$  component (with its  $T_g^A$ ). If this is the actual case, during subsequent heating of the crystallized blocky terpolymer the four transition temperatures  $T_g^C$ ,  $T_m^C$ ,  $T_g^A$ , and  $T_g^B$  should be observed in the DSC curve, together with some degree of crystallinity of the  $(C)_p$  component –  $w_c^C$ . All the experimental results seem to be in favor of the transitions described above and illustrated by the models in Figs. 8 and 9.

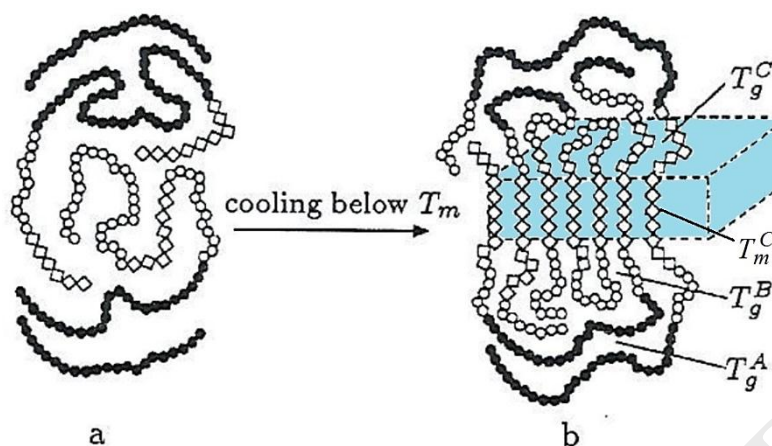


Fig. 9. Schematic representation of the crystallization and dephasing of a block tercopolymer taking place during cooling of the melt. The symbols are the same as in Fig. 8.  $T_g$  and  $T_m$  are the glass transition and melting temperatures of the respective components  $(A)_n$ ,  $(B)_m$ , and  $(C)_p$  [57]. *Source:* Fakirov S, Sarkissova M, Denchev Z. Sequential reordering in condensation copolymers. 3. Miscibility-induced sequential reordering in random copolyesteramides. *Macromol Chem Phys* 1996;197:2889-2907. Copyright 1996 Wiley-VCH Verlag GmbH & Co. KGaA.

Analyzing the system PBT/PC/PAr, we considered the merging of the two  $T_g^{\text{PC}}$  and  $T_g^{\text{PAr}}$  into a single  $T_g^{\text{PC-PAr}}$  (Fig. 7f) as a reliable proof of randomization of this binary blend. The next major step is the randomization of the terpolymer, as illustrated in Fig. 8b. This effect takes place after longer annealing at higher temperature (Fig. 7j). The third stage is the regeneration of blocks by an even longer thermal treatment at the same elevated temperature, as shown schematically in Fig. 8c. Evidence of the occurrence of this transition can be found in the appearance of two glass transitions and one melting temperature, in accordance with our expectations. Note in Fig. 7k the transitions  $T_g^{\text{PBT}}$  and  $T_m^{\text{PBT}}$ , as well as  $T_g^{\text{PC}}$  [53].

In Fig. 9, the corresponding generalized designations are  $T_g^C$ ,  $T_m^C$ , and  $T_g^A$ . The only missing temperature is  $T_g^{\text{PA}}$ , corresponding to  $T_g^B$ , most probably because of overlapping with the melting peak of PBT. Bearing in mind the miscibility of PBT and PAr, one should expect only one  $T_g^{\text{PBT-PAr}}$  instead of two  $T_g^{\text{PBT}}$  and  $T_g^{\text{PAr}}$ . This is not the case because most probably the crystallization of PBT leads to separation of the amorphous PBT and PAr phases [53].

The trend of the miscible components to mix, which acts in a direction opposite to that

of the entropy, also exists at the very beginning of the randomization process, but this trend is obviously too weak to suppress the entropy effect. It may become effective and govern processes for which the entropy increase is small, for instance, the last stages of randomization. Only in this way can one explain why complete randomization via transreactions requires such extremely long times or - the most frequent case - why the randomization ceases at triads and tetrads. Further on, the antagonism between the entropy and other factors during sequential reordering in condensation copolymers can cause effective reversible transformations only if the homopolymer sequences are short enough, i. e. if the block copolymer can be considered as a microblock copolymer.

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 [58,59]. For some cases it has been used also wide-angle X-ray scattering [56].

In summary, the repeatedly reported randomization of molten block copolycondensates is observed 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 by annealing of random copolycondensates and attributed to regeneration of crystallizable blocks. This *crystallization-induced sequential reordering* is driven by upsetting the random  $\rightleftharpoons$  block copolymer 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 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 crystallizable component. Of course, the absence of melting (crystallization) should not be considered as an indication of complete randomization [53].

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. [54,56,57], respectively. They were not only well accepted and widely used but were also proven correct through computer modeling and further experiments (e.g. [60]).

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.

## **6. Additional condensation and transreactions in polymer science and technology**

### *6.1. Relationship between interchain reactions and structure of condensation polymers*

Porter et al. [36] in his review on compatibility and transesterification in binary polymer blends, stressed that a fascinating feature of the blends of the polyester family is their easy transesterification, which has the following consequences: (i) it can open a new route to enhanced compatibility and preparation of novel copolymers with specific degrees of randomness and compositions; (ii) it can lead to more uniform polymers by minimizing molecular weight fluctuations in the melt stream during polymerization and processing; and (iii) it can provide for chemical healing of laminates of condensation polymers [61].

High-performance polymer materials are distinguished by a structure usually involving (i) maximal orientation of macromolecules, (ii) perfect crystallites built up of extended chains, and (iii) a relatively high molecular weight of the polymer. The lower ability of condensation polymers, as compared to polyolefins, to form such a structure is related to their peculiarities - larger cross-section of the macromolecules, more irregular chain



structure, lower molecular weights. The desired supramolecular structure is usually achieved by thermal and mechanical (orientation) treatments [61].

During thermal treatment at elevated temperature, together with structural changes (crystallization and relaxation) condensation polymers undergo the above described chemical interactions; this contrasts with polyolefins, where only degradation could take place. Additional condensation and trans- (exchange) reactions can be used to eliminate defects in the structural entities, originating from chain ends, entanglements and chain folds, as shown schematically in Fig. 10. It should be added here that, in addition to the molecular weight increase, additional solid-state condensation results in the rise of the number of tie molecules.

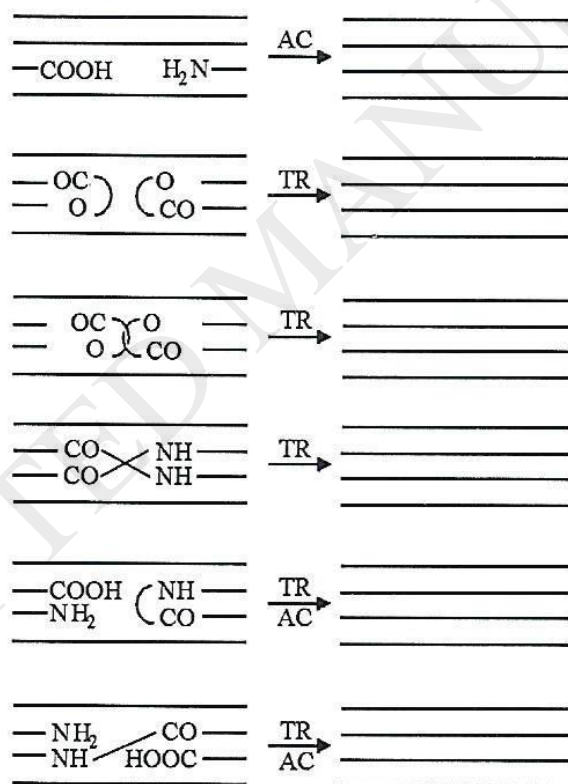


Fig.10. Schematic representation of elimination of defects through solid-state reactions in linear polycondensates: AC additional condensation; TR transreactions [61]. *Source:* Balta Calleja FJ, Fakirov S, Zachmann HG, Effect of transreactions and additional condensation on structure formation and properties of condensation polymers. In: Fakirov S. editor. Transreactions

in Condensation Polymers. Weinheim: Wiley-VCH. 1999. p. 429-479. Copyright 1999 Wiley-VCH Verlag GmbH & Co. KGaA.

In contrast to the chemical aspects of solid-state reactions, their role in the creation of the physical structure in condensation polymers is rather underestimated even today. As emphasized by Wunderlich a couple of decades ago [43] the physical structure leading to optimal mechanical parameters should be characterized by chains stretched as much as possible, of the highest molecular weight, perfectly aligned to each other. Solid-state reactions are expected to contribute to the fulfillment of these requirements by the achievement of maximum molecular weight values and creation of a perfect structure by elimination of defects (Fig. 10). For example, such a structure can be realized by two-stage cold drawing, each stage followed by elevated temperature annealing [62]. After the first cold drawing (up to  $\lambda = 5$ ), the polymer is subjected to annealing in vacuum at a temperature  $T_a$  close to but below the melting one ( $260^\circ\text{C}$  in the case of PET). In addition to crystallization and relaxation, chemical reactions take place during this treatment, resulting in the elimination of defects (Fig. 10) as well as in an increase in molecular weight, and hence in improved drawability [62].

When an oriented and annealed, partially crystalline, high molecular weight material is subjected to a second drawing conformational changes related to the complete extension (at moderate stresses) of the chains in the amorphous regions are affected along the direction of the external strain. Further drawing could result in the destruction of crystallites by chain defolding and alignment in the draw direction.

In view of the practical application of polycondensates with improved mechanical properties, evidence has been provided about the extent to which the above processes occur using wide- and small-angle X-ray scattering (SAXS) as well as mechanical tests. The results of the mechanical tests of samples with different draw ratios ( $\lambda = 5$  or 20) are presented in Table 1. It is seen that the samples with  $\lambda = 5$  annealed at  $260^\circ\text{C}$  for 6 h show an extremely high deformation ability ( $\lambda = 320$ , Table 1, Sample 3) indicating that, under these conditions, the additional condensation and exchange reactions have taken place with a subsequent rise in the molecular weight. Considering that the five-fold drawn samples are subjected to a second drawing at room temperature (after annealing at  $260^\circ\text{C}$ ), the total draw ratio



amounts to  $\lambda = 20$ . It is seen in Table 1 that the tensile strength and elastic modulus of the samples with  $\lambda = 20$  are almost twice as high as those of the samples with  $\lambda = 5$  ( $\sigma = 0.51$  GPa and  $E = 13.8$  GPa against  $\sigma = 0.22$  GPa and  $E = 9.3$  GPa, Table 1, Sample 1). After annealing at 200°C, the samples with  $\lambda = 20$  demonstrate the superior values of  $E = 18.6$  GPa and  $\sigma = 0.60$  GPa [61].

Table 1. Mechanical tests of drawn PET bristles annealed under constant strain [61]

$\lambda = 5$ , annealed for 6 h					$\lambda = 20$ , annealed for 2 h		
Sample no.	$T_a$ (°C)	$\sigma$ (GPa)	$E$ (GPa)	$\varepsilon$ (%)	$\sigma$ (GPa)	$E$ (GPa)	$\varepsilon$ (%)
1	Unannealed	0.22	9.3	61	0.51	13.8	17
2	200	0.26	11.5	38	0.6	18.6	16
3	260	0.14	6.5	320	0.57	16.7	18

These substantial differences in the mechanical properties of both materials are mainly due to the relatively larger number of chains under stress bearing the external strain, as well as to the strong molecular interactions in the highly oriented material. This statement is also supported by the fact that the samples with  $\lambda = 20$  show a rather low and constant elongation at break (16-18%) regardless of the annealing temperature, in contrast to the case of  $\lambda = 5$  (38-320%). In this way solid-state interchain reactions contribute to the improvement of the mechanical properties of polyester and polyamides mainly through the elimination of defects and increase in molecular weight [61].

## 6.2. Compatibilization phenomenon in polymer blends and composites

Blends of different polymers may represent a valid alternative for production of materials with new characteristics without designing new synthesis that are often complex, expensive, and with a high environmental impact. Therefore, by using proper apparatuses and procedures, it is possible in principle to easily obtain new materials with simpler processes and lower costs than are associated with the preparation of completely new materials. Unfortunately, a key factor in blending different polymers is that in most cases they are immiscible and incompatible. That is they display a gross morphology with particles of the dispersed component poorly adherent to the matrix and poorly distributed into the continuous component thus affecting negatively the mechanical performance

of the blend. In these cases, an appropriate compatibilizing system can significantly improve the morphology, and thus the mechanical properties. Among the available thermoplastic polymers, the combination of polypropylene (PP) with PET offers many advantages. The tensile strength of PP is high enough for common textile and technical applications. Its Young's modulus, however, has a low value that limits its applications [63].

Few polymers form truly miscible blends characterized by a single glass transition temperature and homogeneity on a 5-10 nm scale with domain sizes comparable to the dimension of a macromolecular statistical segment. Most blends are immiscible, i. e., possess a phase-separated morphology. Blends of this type are often preferred over the miscible ones since they combine some of the important characteristics of both blend components. Blend composition, viscoelastic properties of the components, and interfacial adhesion are among the parameters known to control the size and morphology of the dispersed component and its stability to coalescence. Heterogeneous blends of technological importance are termed "*compatible*" and they constitute most of the commercial blends introduced in the past 50 years. In such blends, often known also as *alloys*, satisfactory physical and mechanical properties are related to the presence of an interphase modified through compatibilization and the formation of a fine dispersed morphology resistant to phase separation.

Compatibilization in polymer chemistry is the addition of a substance to an immiscible blend of polymers that will increase their stability. Polymer blends are typically described by coarse, unstable phase morphologies. This results in poor mechanical properties. Compatibilizing the system will make a more stable and better blended phase morphology by creating interactions between the two previously immiscible polymers. Not only does this enhance the mechanical properties of the blend, but it often yields properties that are generally not attainable in either single pure component.

Polymer compatibility, which may lead ultimately to complete thermodynamic miscibility, may be enhanced by various methods. In addition to co-crystallization and co-cross-linking, strong interactions such as acid-base or ion-dipole, hydrogen bonding and transition metal complexation between suitably functionalized components, have been shown to improve compatibility [64]. More commonly, compatibility is promoted through interfacial active copolymers (e.g., block, graft, random) with segments capable of specific

interactions and/or chemical reactions with the blend components. Block or graft copolymers are commonly used as compatibilizing agents. The copolymer used is made of the two components in the immiscible blend. The respective portions of the copolymer can interact with the two components of the blend to make the phase morphology more stable. The increased stability is caused by reducing the size of the phase-separated particles in the blend. The size reduction comes from the lower interfacial tension, due to accumulating block copolymers at the many interfaces between the two copolymers. This helps the immiscible blends break up into smaller particles in the melt phase. In turn, the separated particles will not be as inclined to consolidate and grow because the interfacial tension is now much lower. This stabilizes the polymer blend to a usable product. An example are ethylene/propylene copolymers. They are able to act as good compatibilizing agents for blends of polypropylene and low density polyethylene. In this specific application, longer ethylene sequences are preferred in the copolymer. This is because co-crystallization also factors into this case, and the longer ethylene sequences will retain some residual crystallinity.

Another compatibilization approach is the reactive compatibilization in which immiscible polymer blends are compatibilized by creating copolymers in the solution or melt state. Copolymers are formed when the proper functional groups in each component of the immiscible blend interact in the compatibilization process. These interactions include hydrogen, ionic or covalent bonding. The functional groups that cause these interactions can be the end groups that are already present in the blend polymers (e.g., carboxylic acids or alcohols on polyesters, or amine groups on Nylons). Another approach is to add functional groups to the component chains by grafting. The many possible functional groups allow for many types of commercial polymer blends, including polyamide/polyalkene blend systems.

The reactive compatibilization has a number of advantages over using the traditional block or graft copolymer as the compatibilizing agent. Unlike the latter approach, reactive compatibilization does not rely on diffusing preformed copolymers. Copolymers are formed at the interfaces of the two immiscible components and do not need to be dispersed. In the traditional approach the system needs to be well mixed when adding the copolymers. Reactive compatibilization is also much more efficient than traditional compatibilization. This is because in reactive compatibilization, functional groups are either already present, or easily grafted on the

blend components. In the traditional compatibilization, copolymers must be synthesized on a case by case basis for the components to blend [65].

A list of possible transreactions between polyesters, polyamides, and their combinations that could lead to the formation *in situ* of interchain copolymers is shown in Table 2. Reactions include direct interchange of groups present in the main chains (ester/ester, amide/amide and ester/amide) only.

Table 2. Possible transreactions between polyesters, polyamides and their combinations

Reaction type	Reactive group	Co-reractive group	Transreaction <sup>a</sup>
Ester interchange (transreactions)	Ester	Ester	$A-COO-A + B-COO-B$ $\rightleftharpoons A-COO-B$
Amide-ester exchange	Amide	Ester	$A-CO-NHA + B-COO-B$ $\rightleftharpoons A-CO-NHA + B-COO-A$
Amide-amide exchange (transamidation)	Amide	Amide	$A-CO-NHA + B-CO-NHB$ $\rightleftharpoons A-CO-NHA + B-COO-A$

<sup>a</sup>A and B indicate the respective polymers

Transreactions take place more easily at elevated temperatures required for melt-blending and principally depend on initial component miscibility and blending conditions. These include temperature, mixing time, viscosity match, and the presence of residual catalysts from polymerization (e.g. Ti compounds, Sb<sub>2</sub>O<sub>3</sub> in polyesters) and inhibitors. Transreactions can occur in both miscible and immiscible blends. In the former, miscibility is caused directly only by interaction of components and transreactions may play a secondary role. In the latter, the reactions presumably occur at the interfacial regions between the components.

Several techniques have been used to follow transreactions and differentiate them in terms of their effects on miscibility from strong interactions. Porter and Wang [36] reviewed the application of these techniques in polyester systems. The compatibilization in polymer blends by means of various chemical interactions is discussed in many reviews (e.g. [64]).

Intermolecular reactions of groups in the main chain with terminal end-groups or side groups are of interest in the recent time particularly because of the wide application of polypropylene as composite component (mostly as matrix).

Polypropylene is one of the most important plastics as it has an excellent balance of mechanical properties, melt flow, color stability, chemical resistance and moisture barrier properties together with low cost. However, critical disadvantages for wider application of this material are its minimal impact strength and non-polar and inert nature which result in difficulties in blending, coating and inking. As a matter of fact, PP as a homopolymer is outside the scope of this review but functionalization of PP with polar molecules is an attractive method to improve the properties of this material. By far, maleic anhydride (MA) is the most important molecule in this context and MA modified PP has been prepared for commercial purposes and used to improve the polarity, compatibility and interaction of polypropylene with other materials [66]. The grafting reaction normally is carried out by a radical mechanism.

Maleic anhydride has been also used for grafting atactic polypropylene (aPP) acting as a typical compatibilizer for synthesis of poly(ethylene-co-octene) organically modified montmorillonite nanocomposites. The maximally grafted aPP (93.67% with 3 wt. % MA) was used for compatibilization [67].

Maleic anhydride is highly reactive with a great variety of polymer chains and biological macromolecules, as protein, lipid and glucose [67]. The MA groups grafted to the polymer may react with the reinforcement agent functional groups, resulting in grafted copolymers. The use of MA grafted to thermoplastics as polyethylene and polypropylene improves the interfacial adhesion between the matrix and some reinforcement agents, such as oak wood flour [68], bamboo pulp fiber [69], kenaf fiber [70], and others. It was observed that the presence of the compatibilizing agent induces a stronger interfacial adhesion and improvement of the mechanical properties, compared to non-compatibilized composites [70].

It is important to stress that the addition of fillers or nanofillers for reinforcement of polymeric matrixes needs always the analysis of interfacial region between filler and polymer matrix, since the compatibility between these components determines the final properties of composites and nanocomposites. It is through the interfacial region that occur the strain transfer from the matrix to the reinforcement agent. When there is no compatibility, the interfacial region is the weaker region of the composite. Where the failure occurs, it is due to inefficient strain transfer.

### 6.3. *Exchange reactions and additional condensation in polymer-polymer composites*

The environmental concern caused by plastic materials is steady progressing as demonstrated by the very recent decision of the European Commission [71]. The Commission is proposing new EU-wide rules to target the 10 single-use plastic products most often found on Europe's beaches and seas, as well as lost and abandoned fishing gear. Together these constitute 70% of all marine litter items. The new rules are proportionate and tailored to get the best results. This means different measures will be applied to various products. Where alternatives are readily available and affordable, single-use plastic products will be banned from the market. For products without straight-forward alternatives, the focus is on limiting their use through a national reduction in consumption; design and labelling requirements and waste management/clean-up obligations for producers. It is believed that the new rules will put Europe ahead of the curve on an issue with global implications [71].

This step of the European Commission [71] makes clear why during the last two decades studies aiming at replacement of the mineral reinforcing component in polymer composites resulted in creation of new types of composite materials. To them belong the polymer–polymer composites with natural fibers as reinforcement [72] or synthetic fibrous components as reinforcement [73], as well as the single polymer composites suggested by Capiati and Porter [74] being an increasing attraction for academia [75-84], and industry (e.g. [85]) (for example, the commercialized product Tegriss developed by Milliken [86]). The use of synthetic, petroleum-based polymers as reinforcement is not as advantageous as using natural fibers that are biodegradable and eco-friendly. Also, the synthetic polymer–polymer composites seem to be much more acceptable from the environmental point of view in contrast to their inorganic counterparts because they, being organic in nature, could be subjected to incineration.

The single polymer composites are an even better solution than polymer–polymer composites. They can be melted down to a single polymer, which can then be used in the manufacture of another single polymer composite, used in a regular composite, or any other application for that polymer.

Although recycling is becoming increasingly important to consider, the primary concern for most composites is still achieving the desired mechanical properties. But a widespread problem with many polymer composites is that the strength of the reinforcement is not fully utilized as the

matrix and reinforcement do not have perfect adhesion. The problem of adhesion arises, because typically the word composite describes a combination of matrix and reinforcement which are chemically different. As a rule, they find it difficult in varying degrees to bond together. Creating polymer-polymer composites is one possible solution as polymers are much closer chemically to each other than their mineral counterparts, and so easier to choose for good adhesion. For example, while both component in these composites are hydrophobic, in the glass fiber reinforced polymer composites the matrix is hydrophobic and the reinforcement – hydrophilic [82].

Particularly favourable opportunities for extreme improvement the adhesion quality in the case of polymer-polymer composites are available if the two components are condensation polymers. The latter undergo additional chemical interactions in their melts [3] but also in solid state [12] at elevated temperatures. As discussed above, these reactions are the additional condensation and transreactions [48], eqs. (3) and (4). They result in the formation of a copolymeric layer at the interface playing the role of a compatibilizer, i.e., one deals with a *self-compatibilization effect* [87-93]. There is no need to introduce an extra synthesized copolymer of the blend components thus contrasting the common approach [64]. It must be stressed that the described compatibilization can be effective only in the initial stages of chemical interaction. During prolonged thermal treatment, the reaction goes to completion and finally involves the entire amount of the isotropic (molten) component and the amorphous portion of the fibrillated one in the formation of block copolymers with a sequential order corresponding to the temperature and time of treatment as discussed above [82].

If the main target is simply improvement of interfacial adhesion but not deep chemical changes in the matrix of polymer-polymer composite, a short thermal treatment during the processing of condensation partners is quite enough. This will result in the establishing of chemical bonds between the blend components or matrix and reinforcement (in case of polymer-polymer composites).

It should be stressed that the non-condensation polymers could also be involved in similar chemical interactions (except transreactions) if they contain as side groups functional groups as -OH, -COOH, -NH<sub>2</sub> and others. Good examples in this respect are cellulose-based materials. What is more, the effect of these chemical interaction on the mechanical performance of the polymer

composites could be significantly increase if the proceeding of the chemical reaction will be enhanced by the presence of the respective catalyst. For example, a polyamide 6 single polymer composite with layered structure was manufactured using PA 6 high tenacity yarn (reinforcement) and PA 6 film prepared via melt quenching (matrix) [94]. The material shows superior mechanical properties – tensile modulus is improved by 200% and the ultimate tensile strength – by 300–400% as compared to the isotropic matrix film. Further improvement by another 50% has been observed if catalyst has been applied [94].

In author's opinion, the composite community does not exploit this potential for drastic improvement of the interfacial adhesion quality between matrix and reinforcement enough. This is despite the fact that today the polymer materials development in commercial dimension takes place in interdisciplinary groups consisting from engineers, chemists and physicists.

#### **7. Recycling opportunities of condensation polymers based on their chemical peculiarities**

Recycling of poly(ethylene terephthalate) represents one of the most successful and widespread examples of polymer recycling [95-97]. Due to its excellent mechanical properties and chemical resistance, today PET is an irreplaceable material with numerous applications. On the other hand, a continuous increasing consumption along with non-biodegradability of PET waste has led to serious problem of environmental and economic importance. It is considered that recycling processes are the best way to economically reduce PET waste [98].

The various methods of PET recycling include primary, secondary (mechanical), tertiary (chemical) and quaternary methods [96,97]. Primary recycling refers to the in-plant recycling of the scrap material of controlled history, that is, reuse of products in their original structure. This method is easy to perform and low cost, but dealing only with clean, uncontaminated, single-type waste. Energy recovery or quaternary recycling refers to the recovery of energy that is contained in a polymer, and this is currently the most effective way to reduce the volume of organic materials together with considerable yield of energy. However, in some respects this method is ecologically unacceptable owing to the health risk from airborne toxic substances [99].

Currently, the dominant form of PET waste recycling worldwide is mechanical recycling which means the reprocessing of waste plastics by physical means, like cutting, shredding, washing, and so on, into plastic products. Mechanical recycling requires homogenous plastics and relatively



clean material. However, the powder obtained by mechanical recycling, due to the degradation, which occurs during each cycle, shows a decrease in physical properties compared to virgin PET and it is not suitable for bottle products. The molecular weight of the recycled polymer is reduced because of chain-scission reactions caused by the presence of water and traces of acidic impurities. Through mechanical recycling, waste PET bottles can be found in films, sheets, strapping packaging, and fiber used for sacking and their usage for insulation and for floor covering has also been studied [100,101].

Strategies for maintaining the high average molecular weight of polymer during reprocessing are also studied and include intensive drying, reprocessing with vacuum degassing and the use of chain extender compounds [102]. A good example in this respect is the increase of molecular weight of Nylons via additional solid state polycondensation.

#### *7.1. Application of additional solid-state condensation for recycling purposes*

It is well known that in the production of polyamide and polyester fibers, wastes amount to 10% of the total production [103]. In the production and processing of polyester films, wastes are some 30% or more [104]. These wastes are often hydrolyzed to recover the monomers or burnt for energy production. Wastes from PA 6 fiber production are mostly used in injection molding, although, owing to their low molecular weight, they have poor processing and operational properties. These disadvantages can be avoided by carrying out an additional solid-state condensation, resulting in a molecular weight increase. As a first consequence, such a treatment increases the melt viscosity and thus improves the processing properties [61].

It is demonstrated with PA 6 wastes that, after regranulation and heat treatment in vacuum for different periods of time (10 to 50 h), the molecular weight grows from 18000 to 40000. Fig. 11 shows the effect of molecular weight on the stress at break,  $\sigma_b$ , for PA 6 wastes subjected to an additional solid-state condensation [105]. It is obvious that the molecular weight increases from 19000 to 30000 leads to a 55% increase in the stress at break. A further molecular weight increase to 40000 does not affect the tensile strength. It is worth noting that the maximal strength value of this secondary material (660 kg/cm<sup>2</sup>) is significantly higher than that of the fresh material used for fiber production ( $\sigma_b = 550$  kg/cm<sup>2</sup>) [105].

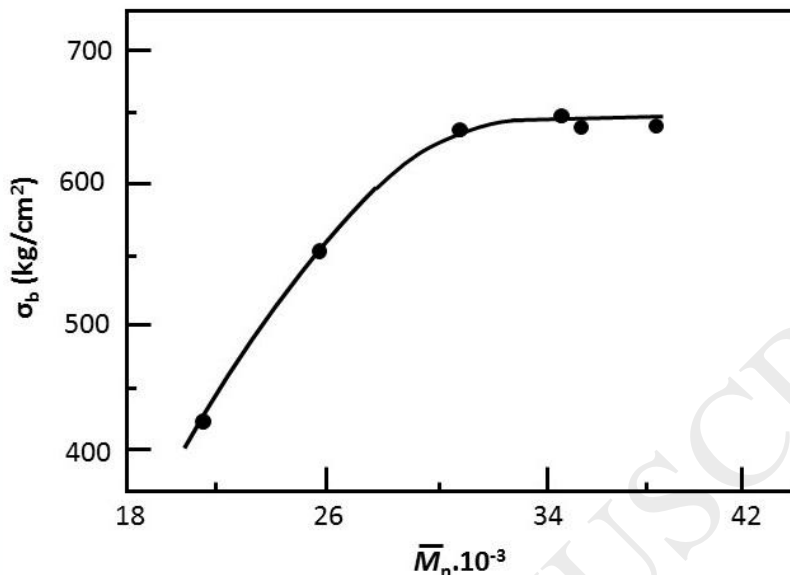


Fig. 11. Dependence of the stress at break  $\sigma_b$  on the molecular weight  $M_n$  achieved by additional solid-state condensation under vacuum at 210°C for various durations from PA 6 processing wastes.

The conclusion is that additional solid-state condensation is a useful tool for the recycling of wastes from the production of polyamide and polyester films and fibres. By increasing the molecular weight of these wastes, materials are obtained that have processing, mechanical, and operational properties typical of engineering plastics.

Simplicity is an important characteristic of this recycling method. There is no need to use, remove, or regenerate solvents, or to add other reactants. There is no need to melt, stir, and regranulate the polymer. Furthermore, during additional solid-state condensation there is almost no by-product formation, or, if any are formed, they are innocuous (water or glycols) and in minute quantities. It is for this last reason that additional solid-state condensation raises no environmental problems. Therefore, this recycling belongs to the category of wasteless technologies and is very promising [61].

## 7.2. Chemical recycling of PET waste

In the introductory part of this review, it was mentioned that a characteristic feature of the polycondensation process is the fact that the formation of a polymer is paralleled by separation of a low molecular weight product (usually water, as shown in eq. (1)). What was not mentioned there

is that this process has another important characteristic feature – it is reversible, that is the polymer in the presence of the respective low molecular weight product and the essential reaction conditions (temperature, catalyst, etc.) can be converted back into the starting monomers:



The reversibility of polycondensation reactions is an inherent fundamental characteristic feature of all condensation polymers. The occurrence of the above reaction (eq. (5)) during processing and exploitation of condensation polymers results in reduction of polymer molecular weight and subsequently in strong degradation of their mechanical performance. The most common process of this type is the hydrolysis and for this reason the processing of condensation polymers in their melts must be preceded by careful drying. For PET the moisture content must be reduced to below 0.02% [97]. The same holds for polyamides particularly because their ability to absorb a couple of percent of moisture at ambient conditions.

In some cases, these “negative” characteristics of condensation polymers can be considered as quite positive, for example in solving recycling problems. They offer the opportunity for chemical or feedstock recycling (tertiary recycling), which involves transformation of polymer chains. In fact, this is a process leading to the total or partial degradation of the polymer backbone to the monomers (i.e., depolymerization) or to oligomers or larger chain fragments (i.e., random chain scission) and other chemical substances, which are mainly gaseous products. The chemical recycling is carried out either by solvolysis or by pyrolysis. The solvolysis occurs through degradation by different solvents, while the pyrolysis occurs through degradation by heat in absence of oxygen or air or in a vacuum. Chemical recycling yields monomers, petroleum liquids and gases [106]. Monomers are purified by distillation and drying, and they could subsequently be repolymerized to regenerate the original polymer [107].

In a large collection of researches of the chemical recycling of PET, the primary objective is to increase the monomer yield while reducing the reaction time and/or carrying out the reaction under mild conditions. Continuous efforts of researchers have brought about great improvements in the chemical recycling processes [108].

Depending on the low molecular weight product involved in the degradation process, the chemical recycling can be categorized as hydrolysis, alcoholysis, acidolysis, etc. Below are listed some of them with some more details.

*Methanolysis.* Methanolysis of PET consists of the degradation by methanol at relatively high temperatures (170-280°C) and pressures (20-40 atm). The main products of PET methanolysis are dimethyl terephthalate (DMT) and ethylene glycol (EG), which are the monomers for the PET synthesis [109,110]. The process is described in patent literature [111,112].

The main advantage of this method is that an installation of methanolysis can be in the polymer production line, where waste PET arising in the production cycle is used and the monomers recovered can be re-used in the manufacture of a full value polymer. Disadvantages of the method include the high cost associated with the separation and refining of the mixture of the reaction products (glycols, alcohols and phthalate derivatives).

*Glycolysis.* The simplest method of PET depolymerization, which is widely used on a commercial scale in many companies worldwide such as DuPont, Goodyear, Shell Polyester, Zimmer, Eastman Kodak and other, is the glycolysis reaction [113]. The glycolysis represents the molecular degradation of PET polymer by glycols, in the presence of typical transesterification catalysts, mainly metal acetates, where ester linkages are broken and replaced with terminal hydroxyl groups, either under pressure or at atmospheric pressure. The method involves a transesterification reaction of PET with an excess of glycol at temperatures in the range of 180-240°C.

Glycolysis of PET waste proceeds through at least three stages: oligomers, dimer and monomer. The glycol diffuses into the polymer, causing the polymer to swell up, thus increasing the diffusion rate. The glycol subsequently reacts with an ester bond in the chain and degrades the PET into lower fractions [114].

Various experimental factors include temperature, pressure, reaction time, as well as stirring speed, particle size, a choice of solvent and its ratio [115,116]. Besides metal acetates, there are various catalysts which can be used in PET glycolysis, such as ionic liquids [117-120], urea [121], metal oxide nanocomposites [122,123] or hydrotalcit [124].

*Aminolysis.* Aminolysis is the reaction of PET with different primary amine aqueous solutions such as methylamine, ethylamine, ethanolamine and anhydrous n-butylamine in the temperature range of 20-100°C. This is done to yield the corresponding diamides of terephthalic acid (TPA) and EG [113]. PET in the form of waste fibres and disposable soft drink bottles were subjected to

depolymerization through aminolysis using excess of ethanolamine in the presence of glacial acetic acid, sodium acetate and potassium sulphate as catalysts. The maximum yields under optimized conditions were 91.1% from PET fibrous waste and 83.2% from bottle waste. In the absence of any catalyst, the yield was only 52%. This difference in the yields was attributed to the molecular weight and its distribution in PET fibrous waste and the bottle waste. For the fibre grade PET, the molecular weight is lower and the molecular weight distribution is narrower than that for the bottle grade PET in order to attain higher viscosity for the latter, necessary for the blow-molding process [125].

*Ammonolysis.* Ammonolysis is the reaction of ammonia with PET to produce a terephthaldiamide (TPDA). This can be converted to terephthalonitrile, and further, to other chemical substances. Very good results were obtained from the ammonolysis of PET waste from postconsumer bottles. The process was carried out under a pressure of about 2 MPa in a temperature range of 120-180°C for 1-7 h. The TPDA can be converted into terephthalic acid nitrile and further to p-xylylenediamine or 1,4- bis(aminoethyl)cyclohexane [107].

*Hydrolysis.* Hydrolysis is a method of PET waste recycling in which PET is reacted with water in acidic, basic or neutral condition, leading to complete depolymerization and resulting in its monomers, TPA and EG. The hydrolysis reactions require the use of high temperature (200-250°C), as well as relatively high pressure and long time needed for complete depolymerization. Commercially, hydrolysis is not widely used, because of the cost associated with purification of the recycled TPA.

Alkaline hydrolysis of PET is usually carried out with the use of an aqueous alkaline solution of NaOH or KOH, in the concentration of 4-20 wt. % [126]. The factors which have a great effect on the kinetics of the alkaline depolymerization of PET in NaOH solution are temperature, time and alkali concentration, as well as the choice of solvent. The main advantage of alkaline hydrolysis in comparison with the other methods of the chemical recycling is that it can tolerate highly contaminated, postconsumer PET such as magnetic recording tape, metallized PET film or photographic film (X-ray film). The process is relatively simple and less costly than methanolysis [113].

Acid hydrolysis is performed most frequently using concentrated sulfuric acid, although other concentrated mineral acids (e.g., phosphoric or nitric acid) can be used. Acid hydrolysis of PET in sulfuric acid at different temperatures and solution concentrations was reported [114]. Neutral hydrolysis is carried out with the use of water or steam in the presence of alkali metal acetates as transesterification catalysts. Low purity of TPA is the major drawback of this method. Hydrolysis is comparatively slow because water is a weak nucleophile [107,113].

*Enzyme Catalyzed Hydrolysis.* Recently, the recycling methods based on enzyme catalysis have been provided with many advantages compared to classical chemical processes. Advantages of enzymatic methods include the fact that their action under mild conditions with low energy input without the need for expensive machinery might be helpful in PET degradation [115]. Recently, [127] a novel bacterium was isolated, that can use PET as its major energy and carbon source. When grown on PET, this strain produces two enzymes capable of hydrolyzing PET and the reaction intermediate, mono(2-hydroxyethyl) terephthalic acid. Both enzymes are required to enzymatically convert PET efficiently into its two environmentally benign monomers, TPA and EG.

## 8. Conclusions

Analyzing the related with the specific for condensation polymers only chemical interactions, the additional condensation and trans- (exchange-) reactions, phenomenon of *chemical healing*, that is self-repairing as a result of these reactions, together with the phenomenon of *physical healing* when the physical diffusion only leads to self-repairing, it is concluded that these two cases only belong to the category of “*self-healing*”. The rest of cases of self-repairing when a chemical treatment of the sample before or during its repairing is needed belong to the category of “*chemically assisted healing*”. Obviously, the terminology about self-repairing materials needs to be reconsidered.

Quite similar seems to be the situation with the diffusion mechanism in condensation polymer systems particularly at elevated temperatures – the widely used *reptation model* must be complemented by the phenomenon of *chemically released diffusion*, that is mass transfer paralleled by transreactions when parts of one molecule are moved to another one and being incorporated in this second molecule. It follows that dealing with condensation polymers, in addition to the classical case of physical diffusion

when the entities of the mass transfer are the whole molecules, another type of mass transfer is also possible – transfer parts only of macromolecules from one to another macromolecule.

The discussion of the widely studied cases of sequential reordering in condensation copolymers is based on the understanding that the respective sequential order is not determined by the interchange reactions. The additional condensation and mostly the trans- (exchange-) reactions are only a tool for realization of one or the other sequential order. The latter is determined by other factors in the system as entropy, enthalpy, miscibility, and others, or more precisely, which of these factors dominates at a given set of conditions.

The main task of this review was to demonstrate that some basic knowledge as the characteristic for condensation polymers only chemical interactions (by the way, forgotten by polymer chemists as very primitive and unknown for engineers) can still be helpful in the search of polymer material with improved properties. Looking for new materials the researchers should not neglect these opportunities since sometimes the new rather promising approaches do not meet the expectations. The best example in this respect is the mechanical performance of polymer nanocomposites - it is rather modest – improvements (if any!) of elastic modulus by 20% and the tensile strength by 50% are typical [128-132]. Generally, these systems showed 10 – 35 % improvement in mechanical properties with 0.2 – 5 wt. % filler [132]. However, *“the translation of these improvements to prepregs or laminates proved to be difficult due to processing issues, including extremely high viscosity, nanoparticles filtration, nanoparticles agglomeration, and void formation”* [132].

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