PART I

INTRODUCTION

Chapter 1

Creation and Development of Thermoplastic Elastomers, and Their Position Among Organic Materials

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The thermoplastic elastomers (TPEs) concern large industrial and commercial fields, as well as academic and applied research. Often the TPEs are considered as being only an important part of the block copolymers, but they are present in many other polymeric materials, as clearly shown by Holden *et al.* [1,2] and Rader [3–5]. They are characterized by a set of properties inherent to block and graft copolymers, different blends, and some vulcanized materials. More than 7000 *Chemical Abstracts* entries directly concern TPEs and in about 12500 other publications they are closely associated to other issues (*SciFinderScholar*) [6]. Most of these references describe materials, which associate elastomeric recovery and thermoplastic properties; however some products exhibit characteristics and properties, which completely differ from those of conventional TPEs.

Historic, scientific, technical and commercial considerations [2–5] should be taken into account when outlining the TPE domain. This introductory chapter begins with historical considerations, followed by a critical evaluation of the main preparations and modern analytical techniques used in chemical, structural, and morphological studies. The TPE properties and processability, their position among organic materials, and their applications are analyzed. Finally, the most probable trends of their future development are discussed in a short conclusion.

1. Birth and development of TPEs: a brief survey

The real era of TPEs began with the advent of block and grafted copolymers. However, some blends are tacitly accepted as TPEs, even though their structure does not exhibit some of their essential characteristics, such as the separation of soft and hard phases; for instance, PVC plasticized by high-boiling liquids is often considered as one of the precursors of the TPEs [7]. The reactions between diols and diisocyanates resulting in polymeric products [8–12] were an important step in the TPE development, since these elastomers exhibit a very rapid elastic recovery and good processability. It is important to stress that these syntheses are two-step processes and their introduction on the market was the result of a new strategy. The latter was rapidly applied to polyesters when Snyder [13] polycondensed a mixture of terephthalic acid, octanedioic acid and propane-1,3-diol and, separately, terephthalic acid with ethane-1,2-diol; these two polycondensates were mixed, then reacted and the ultimate product exhibited elastomeric and plastic properties, was extrudable in the melt and spinnable from solution. In the 1950s, some other elastomers were patented, particularly polyurethanes [14] and, as Snyder's product, they behaved as vulcanized rubber even though they were not chemically crosslinked, as revealed by their complete solubility. All these elastomers exhibited properties which were not observed in natural rubber or in the first synthetic rubbers, but it is important to emphasize that they were prepared by reactions which were already classical at that time. Nevertheless, the advent of these materials generated new researches in chemistry and, perhaps more important, in structure and morphology.

When Szwarc *et al.* discovered [15,16], or rediscovered [17,18], the anionic living polymerization, a completely different preparation of these elastomers was proposed; the study of TPEs passed from infancy to maturity. These authors used sodium metal naphthalene diinitiators to prepare poly(styrene-*b*-isoprene-*b*-styrene), which was probably the first TPE with a perfectly defined structure. However, this copolymer could not be commercialized, as most of the polyisoprene units were -3,4-, with poor elastomeric properties. It is only when the polymerization was initiated by alkyllithium that poly(styrene-*b*-isoprene-*b*-styrene) and poly(styrene-*b*-butadiene-*b*-styrene) were obtained with the classical TPE properties: very high tensile strength and elongation at break, very rapid elastic recovery, and no chemical crosslinking. Bailey *et al.* [19] announced the existence of these materials in 1966 and Holden *et al.* [20] published the corresponding theory in 1967 and extended it to other block copolymers.

In addition to their commercial success, the TPEs were the result of logical considerations and scientific effort, giving birth to a new field of science and technology. These multiphase materials stimulated many theoretical and experimental studies dealing not only with their chemistry, but also with their structure and morphology.

Later, the preparation and the characterization of new TPEs followed; once again, it is important to stress that the arrival of these materials resulted from logical considerations, as it was brilliantly confirmed by the theoretical and experimental studies by Tobolsky, predicting the existence of EPDM [21]. Based on these fundamental studies, many other TPEs were prepared by very different syntheses, commercialized or not, but with many common structural characteristics. In 1962, this new strategy was applied to prepare copolymers containing random poly(ethylene-*co*-propylene) as amorphous blocks and *linear* polyethylene or *isotactic* polypropylene as hard blocks [22]; once more, Tobolsky had predicted that such a copolymer would exhibit TPE properties.

The first polyurethane samples resulted from the pioneering work of Otto Bayer [7] and Christ [12] aiming at the preparation of new textile fibers. Coffey [23] described their elastomeric properties. However, the really scientific approach to thermoplastic polyurethane (TPU) elastomers began with the publications of Müller *et al.* [24] and Petersen *et al.* [25]. The TPU behavior was analyzed by Otto Bayer and his school [26] in a theoretical study where, for the first time, a truly linear polyurethane was prepared through a sequence of steps, announcing the classical route used to obtain thermoplastic polyurethanes: preparation of an α,β-diisocyanate prepolymer, resulting from the reaction of an α,β-dihydroxy-polyester (or polyether) with an excess of diisocyanate, then extended by water with formation of urea linkages, and then reacted with additional diisocyanate. After the importance of the addition of a short-length diol was recognized, the modern chemistry of polyurethanes was definitely born. It was the first case when polyaddition was systematically used and a new strategy was defined, opening the door to many other TPEs. The understanding of the non-chemical crosslinking was perhaps more important than the chemistry; this peculiar observation was first called “virtually crosslinked elastomer” [27]. Soon it became clear that the TPE chains were formed by a succession of long flexible blocks responsible for the elasticity and hard ones interconnecting the macromolecules. It appeared that the blocks were incompatible and localized in separate microdomains. This microphase separation was called “segregation”.

The above fundamental studies were followed by the logical application of the respective strategy to polycondensation, which resulted in the preparation of some very important TPEs: poly(amide-*b*-ester) [28–30], poly(amide-*b*-ether) [31–33], and poly(ether-*b*-ester) [34–36].

Nowadays, the development of TPEs concern many branches of macromolecular chemistry: cationic and radical polymerizations, chemical modification, enzymatic catalysis or the use of microorganisms. Their respective contributions are analyzed in Section 2. The elastomers based on halogen-containing polyolefins [37] and those prepared by dynamic vulcanization [38] are also included in the TPE family. More information on these materials and techniques is given in Section 2.

2. Main routes to thermoplastic elastomer preparation

The chemistry of TPEs continuously changed with time and in this chapter the present-day situation is analyzed with emphasis on polycondensation, polyaddition, and chemical modification, which is often associated with the other processes.

An essential part of this section concerns block copolymers, but the contribution of some other processes, such as grafting or dynamic vulcanization is, by far, not negligible and their current state is discussed.

The synthesis of block copolymers follows two essential pathways: (i) a difunctional oligomer initiates the formation of two or more other blocks (Scheme 1) and (ii) two or several different difunctional oligomers react together or with a coupling agent (see Chapter 2); sometimes, the second block can be prepared in the presence of the first one.

$$\mathrm{A{-}A} \xrightarrow{\mathrm{M_1}} {}^{*}\mathrm{M_1(M_1)}_{\overline{p}}\mathrm{A{-}A{-}(M_1)}_{q}\mathrm{M_1^{*}} \xrightarrow{\mathrm{M_1}} {}^{*}\mathrm{(M_2)_r(M_1)}_{\overline{p+1}}\mathrm{A{-}A{-}(M_1)}_{q+1}\mathrm{(M_2)_t^{*}} \qquad (1)$$

A–A is an initiator

Pathway (1) is mainly encountered in chain polymerization (anionic, cationic, and controlled radical polymerizations); the second one refers essentially to polycondensation and polyaddition. There is no strict distinction between these two sets of techniques, *e.g.*, the difunctional oligoethers used in poly(ether-*b*-ester)s or poly(ether-*b*-amide)s can be prepared by ring-opening polymerization and then polycondensed with the other oligomer (Scheme 2) [39].

$$\mathrm{X{-}(Block\ 1){-}X + Y{-}(Block\ 2){-}Y} \longrightarrow \left[\mathrm{(Block\ 1){-}X'\,Y'{-}(Block\ 2)}\right]_n \qquad (2)$$

2.1. *Living anionic polymerization*

Living anionic polymerization remains an important technique for the preparation of well defined triblock copolymers, such as: poly(styrene-*b*-butadiene-*b*-styrene) and poly(styrene-*b*-isoprene-*b*-styrene) [40], and it was extended to copolymers containing polysiloxane blocks or to poly(α-methylstyrene-*b*-propylene sulfide-*b*-α-methylstyrene) [41]. In many applications, anionic polymerization no longer requires a high vacuum line and often an inert atmosphere is sufficient [42]. The ester block-containing copolymers, such as poly(styrene-*b*-butadiene-*b*-methyl methacrylate), were prepared by sequential anionic polymerization and their morphology and mechanical properties differ substantially from those of the triblock poly(styrene-*b*-butadiene-*b*-styrene). Poly(styrene-*b*-butadiene-*b*-styrene*)* was end-capped by alkyl methacrylate blocks, which leads to a pentablock copolymer [43]. TPEs can also be obtained by anionic ring-opening polymerization (ROP): Sipos *et al.* [44] prepared the biodegradable copolymer poly(L-lactide)-*b*-polyisobutylene-*b*-poly(L-lactide), characterized by two separated glassy phases.

2.2. *Living cationic polymerization*

The use of living cationic polymerization in the preparation of TPEs was reviewed by Kennedy [45] in relation to graft and block copolymers, but the application of cationic polymerization to TPEs began before the arrival of the living techniques. Kennedy and Maréchal [46] reviewed a large part of these elastomers in 1992. Living cationic polymerization was an essential breakthrough, as it was also the case of living anionic polymerization. The approach to this technique was vividly described by Kennedy [47], showing that it follows a three-step progression: (i) controlled initiation, (ii) reversible termination (quasiliving systems), and (iii) controlled transfer. It allows the preparation of block copolymers according to Schemes 1 or 2. The number of articles pertaining to the preparation of TPEs by living cationic polymerization is continuously increasing [48–50]. Many of them deal with styrenic TPEs, but more sophisticated architectures were also synthesized. Kwon *et al.* [49] prepared arborescent polyisobutylene-polystyrene block copolymers where the arborescent polyisobutylene was obtained by living cationic polymerization.

Anionic and cationic polymerizations are often associated. Feldthusen *et al.* [51] prepared copolymers containing linear and star-shaped blocks: a living polyisobutylene chain was prepared by cationic polymerization, its ends were converted into 2,2-diphenylvinyl groups, then metallated and used as initiators of the *tert*-butyl methacrylate anionic polymerization.

2.3. *Controlled radical polymerization*

The discovery of the controlled radical polymerization (CRP) offered additional possibilities in the chemistry of TPEs [52–54]. CRP was used in both graft and block copolymer preparation and extensively reviewed by Matyjaszewski [55] and Mayes *et al.* [56]. It allows the easy preparation of novel environmentally friendly materials, such as polar TPEs; it can be carried out in the bulk or in water and requires only a modest deoxygenation of the reaction mixture. Atom transfer polymerization (ATRP) is one of the most important aspects of CRP; it was developed by Matyjaszewski and rests on an equilibrium between active and dormant species [57]. Moineau *et al.* [58] applied ARTP to the preparation of poly(methyl methacrylate-*b*-*n*-butyl acrylate-*b*-methyl methacrylate).

2.4. *Polycondensation and polyaddition*

Strange enough, so far there are no books entirely devoted to condensation TPEs and the latter are considered only in chapters of more general works. The most important TPEs prepared by polycondensation are the subject of several chapters of this book: polyester-based TPEs, poly(amide-*b*-ethers), polyurethanes, *etc.* However, some less known condensation TPEs are described in Chapter 2: metal-containing macrocycles as monomers, liquid crystalline side chains, metallo-supramolecular block copolymers, as well as the use of enzymatic catalysis or of microorganisms.

Block copolymers can be prepared either by polycondensing a difunctional oligomer, which is often the soft block, with the precursors of the hard block, or by polycondensing or coupling two, or more, difunctional oligomers; this aspect is discussed in Chapter 2.

Many difunctional oligomers are prepared by ionic polymerization and then polycondensed with other functional species. Schmalz *et al.* [59] used a sequential preparation of a TPE with a non-polar soft segment: (i) preparation of α,ω-dihydroxy-[polyoxyethylene-*b*-(hydrogenated polybutadiene)-*b*-polyoxyethylene] (A) by anionic polymerization and (ii) polycondensation of A with dimethyl terephthalate and 1,4-butanediol. Shim *et al.* [60] associated cationic polymerization, chemical modification, and polyaddition to prepare a multiple-arm TPE: (i) preparation of a poly(styrene-*b*-isobutylene) sample (C) by living cationic polymerization, (ii) end-capping of the polyisobutylene blocks by allylic groups (D), and (iii) polyhydrosililation of D with SiH-containing cyclosiloxanes as a core. Sometimes the sequence is reversed: polycondensation, end-capping, and then anionic polymerization [61]. These examples show the importance of the association of chain polymerization with polycondensation.

Some difunctional oligomers are prepared by polycondensation and then used in chain polymerization. However, most of them are applied in block polycondensation or polyaddition: Pan *et al.* [62] prepared difunctional oligosiloxanes by polycondensation of dimethyldichlorosilane with different oligomeric diols, and the polycondensates were then reacted with diisocyanates. Yokozawa *et al.* [63] prepared a well defined poly(*p*-benzamide), with a low dispersity index, using a new polycondensation process, which is discussed in Section 6.

The contribution of the difunctional oligomers to the preparation of TPEs should enjoy an important development; their use is not limited to classical chain polymerization and polycondensation since they can be also applied to less common processes, such as the metathesis. A functional diene, for instance an α,ω-divinyl aliphatic or aromatic ester, is polyadditioned with an α,ω-divinyl-(soft-oligomer) in the presence of a metathesis catalyst, *e.g.,* a ruthenium derivative [64,65].

2.5. ***Chemical modification and grafting***

Chemical modification is an important tool in the production of TPEs and the improvement of their properties [66]. It plays an important role in difunctional oligomer chemistry, particularly the modification of end-groups, which is often necessary in polycondensation or in chain polymerization where difunctional oligomers can be used as macroinitiators. Madec and Maréchal [67] prepared an α,ω-dibenzaldehyde-oligosiloxane by reacting an α,ω-dihydrogensilane-oligosiloxane with 4-allylbenzaldehyde and polycondensed it with α,ω-diamino-oligoamides.

Some functional oligomers were prepared by the degradation of a polymer; for instance, Ebdon and Flint [68] obtained α,ω-dialdehyde-[methyl oligo(methacrylate)] by oxidative cleavage of statistical methyl methacrylate-buta-1,3-diene copolymers.

The chemical modification of a block copolymer can be the essential step in TPE preparation; in this connection, the hydrogenation of unsaturated block copolymers is often an important step [69,70]. Numerous modifications aim to improve the TPE properties or to adapt TPEs to other applications, or to make them reactive to a specific compound.

The development of graft copolymers is by far less important than that of block copolymers; however, they are found in interesting patents [71–73]. Grafting is mainly used to modify the properties of a block copolymer, but it can be applied to a rubber in order to generate rigid side chains. Grafting proceeds through two different pathways: direct reaction of the backbone with a monofunctional oligomer (grafting onto) or polymerization of a monomer initiated by an active group of the polymer (grafting from). Ikeda *et al.* [74] condensed chlorinated butyl rubber with the potassium salt of an α-methyl-ω-hydroxy-polyoxyethylene, which is a "grafting onto" reaction. The resulting TPE is amphiphilic and the grafts form separate crystalline microdomains. In principle, these two techniques are applicable to any polymer, but often the first step is the modification of the chains in order to make them reactive.

Controlled chain polymerization plays an important role in "grafting from", involving cationic [47,75], anionic [76,77], and particularly radical processes [55,78] where ATRP is a powerful tool. Gaynor *et al.* [79] prepared monomers $A{=}B{-}C^*$ where $A{=}B$ is a copolymerizable double bond and C^* is an activated halogen, such as *p*-chloromethylstyrene or 2-(2-bromopropionyl)-ethyl acrylate; they are copolymerized with conventional vinyl monomers, leading to the formation of pendant activated groups used as macroinitiators to prepare graft copolymers. Baumert *et al.* [80] copolymerized an alkoxyamine-functionalized 1-alkene with ethylene and the resulting highly branched polyethylene initiated the controlled radical polymerization of styrene or styrene/acrylonitrile.

2.6. *Preparation by blending*

The chemistry and the structure of the elastomers prepared by blending or dynamic vulcanization greatly differ from those discussed in Sections 2.1 to 2.5, even though they have many common characteristics and properties. The elastomers based on halogen-containing polyolefins are included in very important blends, such as PVC-nitrile rubber, PVC-copolyester elastomers, and PVC-polyurethane elastomers. Their characteristics and properties were comprehensively reviewed by Hofmann [37]. As the other TPEs, these blends combine a good elastic recovery with the properties of vulcanized thermoset rubbers. They can be melt-reprocessed numerous times and exhibit good resistance to heat, oils, and many chemicals. They are single-phase polymers, in contrast to most TPEs, which are two-phase systems, and for this reason they are often defined as "processable rubbers".

2.7. *Preparation by dynamic vulcanization*

Dynamic vulcanization (DV) simultaneously performs the mixing and the cross-linking of a rubber and a thermoplastic polymer. The resulting products are called "thermoplastic vulcanizates" (TPV) and are the subject of various reviews and books [3,38,81]. TPV exhibit the two main characteristics of the

TPEs: a good elastomeric recovery and the properties of thermoplastic polymers. Their preparation, structure, and properties were carefully analyzed by Coran and Patel [38]. Their morphology has many common characteristics with the thermoplastic elastomeric polyolefins and involves a highly vulcanized elastomeric phase uniformly distributed in a melt-processable matrix; Rader [5] compares it to a “raisin pie”. The vulcanization of the elastomer takes place when in a molten plastic. The crosslinking improves several TPE properties: behavior with respect to temperature, resistance to swelling in fluids, compression and tension set, creep and stress relaxation.

DV was applied to different systems, *e.g.*, a diene rubber (EPDM, butyl rubber or natural rubber) is associated with a polyolefin (polyethylene or polypropylene) or an acrylonitrile-butadiene rubber (NBR) sample is associated with a polyamide. The high incompatibility between the elastomer and the plastic may be an important obstacle in the preparation of a dynamically vulcanized material, since the properties of the latter depend on the quality of the dispersion. The dispersity of NBR in polyolefins is very low and a polymeric compatibilizer must be added, which often requires grafting and coupling processes.

3. Techniques used in the characterization of TPEs

The preparation of TPEs is closely related to the control of their structure and morphology, all the more that they are structurally complex systems, requiring accurate, efficient, and rapid analytical techniques. The characterization techniques are applied to the TPEs and their precursors. During the last thirty years, they enjoyed a fantastic development; some of them appeared during the last decade. In the following, they are grouped into analytical branches, but it is essential to keep in mind that most of them are associated with some others.

3.1. *Chromatography*

For a long time, the use of chromatography was mainly limited to the determination of molecular masses and to the qualitative estimation of the heterogeneity of the samples. At present, it is a highly efficient technique giving very accurate values [82–89]. Copolymers are complex macromolecular systems, characterized by two distributions in molecular mass and chemical composition; liquid chromatography used at the critical point of adsorption allows the determination of the molecular heterogeneities (chemical and molecular mass distributions) [83].

The association of chromatography with other techniques is successfully developing and allows, for instance, the determination of the molecular mass distribution of each block, in one run, as well as the respective chemical distribution. Kilz *et al.* [86,87] applied two-dimensional liquid chromatography to complex mixtures containing block copolymers, cycles, and functional oligomers; this technique combines the advantages of high perfoprmance liquid chromatography (HPLC) and size exclusion chromatography (SEC), and provides valuable information on the composition, the functionality, and the molecular mass distribution. Gores and Kilz [88] associated several techniques, such as multiple detection SEC, multi-angle laser light scattering, and viscometry; multiple detection allowed the determination of the chemical composition and distribution. The use of chromatography is certainly not limited to research and has become a method for routine check-up and quality control of industrial TPEs [89].

3.2. *Spectrometric techniques*

They are essential to the study of TPEs, particularly when associated with other techniques.

3.2.1. *FT-IR spectroscopy*

Although by far less used than nuclear magnetic resonance (NMR), the Fourier transform infrared (FT-IR) spectroscopy remains an efficient tool in TPE analysis, *e.g.,* in the investigations of cluster formation in thermoreversible networks [90] or in side-chain liquid crystalline TPEs [91]. FT-IR is often associated with other techniques: NMR [92,93] or X-ray diffraction [94].

Infrared dichroism is a powerful technique to study the evolution of the chain orientation in films, particularly when coupled with photoelastic modulation [95]. FT-IR is a rapid technique that is very efficient in industrial applications, such as weathering [96] or analysis of blends [97].

3.2.2. *NMR spectroscopy*

NMR is essential in TPE characterization and present in most studies; it is often associated with other techniques. This technique allows one to have a deep insight in the structure of the block copolymer chains; for instance, Boularès *et al.* [98] used ^{1}H NMR to determine the ester junctions in poly(amide-*b*-copolyether) chains, which were prepared by polycondensation of α,ω-dicarboxylic-oligoamides and α,ω-dihydroxy-copolyether.

NMR is often used as a routine technique because it is efficient in the control of the TPE purity. Frick *et al.* [99] prepared poly(lactide-*b*-isoprene-*b*-lactide)s and showed that they were not contaminated by free homopolymer and diblock copolymers using ^{1}H NMR coupled with SEC.

Some more specific aspects of NMR are necessary when more detailed studies are required. Cross polarized magic-angle ^{13}C NMR in the solid state was applied to the analysis of the microphases and their scales in TPEs [100]. Impulse NMR provided knowledge of the synergic and antagonistic deviations of the mechanical properties of TPE blends [101].

The determination of accurate molecular mass values of the copolymers and their distribution, as well as of the functionality of difunctional oligomers remains a difficult problem. It is necessary to compare the results of, at least, two different techniques, for instance SEC and titration of the end-groups but, unfortunately, the latter is inapplicable when the chain length is high. NMR is probably one of the most efficient tools in the determination of the end-group concentration, particularly when they are modified. For instance, ^{19}F NMR is used after an α,ω-dihydroxy-polymer is reacted with trifluoroacetic anhydride. In some cases, the end-units are converted into groups, which are fluorescent or adsorbing in the visible or UV light; sometimes they are converted into chemically titratable groups.

3.3. *Scattering techniques*

Lodge [102] and Norman [103] reviewed the use of scattering techniques in the characterization of polymers, particularly block copolymers. Static and dynamic light scattering, small-angle neutron and X-ray reflectivity were analyzed and emphasis was placed on their similarities and differences.

3.3.1. *Static and dynamic light scatterings*

These two techniques are coupled in many studies on block copolymers. The use of dynamic light scattering was reviewed by Stepanek and Lodge [104]; it is an efficient tool to analyze the order–disorder transition in block copolymer melts [105,106]. The static version is often used in studies dealing with aggregation and micellization in solvents [107] and is often associated with the dynamic scattering and other techniques, such as cryoscopy.

3.3.2. *Small-angle (SAXS) and wide-angle (WAXS) X-ray scattering*

SAXS and WAXS are particularly efficient in the study of amorphous polymers including microstructured materials, hence their use in block copolymers (see also Chapters 6 and 7). The advent of synchotron sources for X-ray scattering provided new information, particularly on the evolution of block copolymer microstructures with time resolution below one second. In particular, the morphology of TPEs is most often studied with these techniques; Guo *et al.* [108] applied SAXS to the analysis of the phase behavior, morphology, and interfacial structure in thermoset/thermoplastic elastomer blends. WAXS is often associated with SAXS and some other methods, such as electron microscopy, and various thermal and mechanical analyses. It is mainly used in studies of the microphase separation [109,110], deformation behavior [111], and blends [112].

3.3.3. *Small-angle neutron scattering (SANS)*

SANS is an excellent and non-destructive technique, particularly efficient in the study of order–order and disorder–order transitions. It is very useful in the characterization of the morphology of block copolymers in the ordered state and, in this case, it is complementary to electron microscopy.

Several reviews are devoted to SANS applications to TPEs and block copolymers [113,114] and almost 300 reports describe SANS studies of block copolymers. As far as TPEs are concerned, it is a very valuable technique, particularly efficient in the analysis of disorder in the melt [115] or of macroscopic phase separation [116]; it is also used in blends [117,118] and in processing operations, such as dynamic vulcanization [119] or co-molding [120].

Neutron reflection provides the atom composition of a thin film at different depths. It gives the composition profiles of block copolymers deposited as films on silicon wafers [121]. X-ray reflection is used in the same fields as neutron reflection; these are complementary techniques and often associated with some others.

3.3.4. *X-ray diffraction*

X-ray diffraction remains an important tool in morphological studies, for instance in the investigation of the semicrystalline [122] or liquid-crystalline blocks [123] and of the stretching behavior of TPEs [124,125].

3.4. *Microscopies*

Atomic force microscopy (AFM) has an important development in the structural analysis of TPEs. It was applied to different problems: thermooxidative stability and morphology [126], copolymers with arborescent blocks [127], thermoplastic vulcanizates [128], blends [129], and morphology and orientation during deformation studied both by AFM and SAXS [130].

Transmission electron microscopy (TEM) is most useful to characterize the structure and morphology of TPEs. It is almost always associated with other techniques, particularly SAXS, WAXS, SANS, and AFM. TEM is used in studies of interpenetrating networks [131], morphology and crystallinity of hard blocks [132], structural evolution of segmented copolymers under strain [111], and blends [133].

3.5. *Controlled degradation*

The control of some specific parts of a TPE may provide interesting information on its structure. Sundararajan *et al.* [134] used WCl_6-catalyzed metathesis to prepare poly(HB-*b*-butadiene-*b*-HB) where HB is a rigid block, such as polyphenylacetylene, and the blocks are linked by W atoms; their structure was analyzed by ^{1}H NMR, elemental analysis of tungsten and, more original, by the complete separation of the blocks when the TPE is reacted with benzaldehyde. Valiente *et al.* [135] studied the enzyme-catalyzed hydrolysis of phthalic unit-containing copolyesters, which resulted in an efficient analytical tool for the analysis of the chain structure, particularly for the determination of the block length and their distribution in the chains. Luo *et al.* [136] used pyrolysis-gas chromatography/spectrometry to analyze the microstructure of a polyester-polyether copolymer (TPE).

3.6. *Thermal techniques*

Differential scanning calorimetry (DSC) and other thermal analyses are frequently used in TPE characterization, often as routine methods. DSC is a powerful technique to improve the knowledge of the microphase structure (see also Chapter 18). For instance, Ukielski *et al.* [137] investigated the reversible endothermic processes in thermoplastic multiblock elastomers. DSC and thermo-mechanical analysis (TMA) are often used as complementary to other techniques (particularly spectroscopic analyses) or for providing additional information. Anandhan [119] studied the effect of the mixing sequence of dynamic vulcanization on the mechanical properties and DSC showed that nitrile rubber and the copolymer poly(styrene-*co*-acrylonitrile) are thermodynamically incompatible in blends.

4. Properties and processing of TPEs

The determination of the TPE properties calls for the same techniques as those used for other organic materials, though some modifications may be required; they are listed and discussed in [3]. The information they provide, whatever they are, has a sound meaning only when determined in close correlation with structural analyses. The morphology evolution, when TPEs are subjected to processing, must be carefully followed, and it is particularly important to take into account the specificity of TPE rheology in the melt. Most of the methods listed in Section 3 are essential in the understanding of the TPE properties and their changes [129,138,139].

Many of the processing techniques applied to thermoplastic polymers or elastomers hold for TPEs; a few of them are more specific to these materials. Rader [3] clearly underlined the specificity of their rheology in the melt, particularly that they are highly non-Newtonian, hence more sensitive to shear than to temperature. Nishizawa [140] discussed the recent trends in the TPE molding technology.

4.1. *Injection molding*

Injection molding is by far the most used technique in TPE processing due to its high productivity and because it is a clean process with no waste formation. It is used in a great variety of applications ranging from tubes or foams to finished articles; it can be applied to the co- or insert-injection. The use of hot runner methods in injection molding was reviewed by Lachmann [141] and this is an interesting diversification of the conventional technique; it maintains the flowability of the melt during its transportation to the individual cavities or to the individual gates. During injection molding, TPEs behave as the other thermoplastics in hot runner without major problems.

4.2. *Compression molding*

Compression molding is by far less used than injection molding. Akiba [142] reviewed this processing method concurrently to other techniques: injection molding, extrusion, transfer molding, *etc.*

4.3. *Extrusion*

The extrusion of TPEs was reviewed by Knieps [143]. This processing technique is essential in the shaping of many different profiles; the use of single-screw extruders is predominant, but some other extruders are used, such as those equipped with three-section or barrier screws. Extrusion is also applied to other shapes: foams, tubes, sheets, *etc.*

4.4. *Blow processings*

Extrusion and injection blow molding of TPEs are particularly important whatever the shape: bottles, boots, *etc.* They were reviewed by Nagaoka [144], who showed that the parameters controlling the processing are similar to those which control extrusion and injection molding. Blow processes are also used to prepare TPE foams; Brzoskowski [145] prepared low-density foamed thermoplastic vulcanizates, using a single screw.

4.5. *Thermoforming*

The number of references relative to the thermoforming of TPEs drastically increases, particularly in the last three years; most of them are patents and apparently this TPE processing technique does not enjoy so far a general appreciation.

4.6. *Reactive processings*

The corresponding literature was reviewed by Prut and Zelenetskii [146] and an important part is related to dynamic vulcanization; some of the references provide a deep insight in the chemical evolution, particularly in side reactions [147,148]. The morphology of thermoplastic vulcanizates during processing drastically depends on temperature and shear and, to a lesser extent, on the screw rate [149].

4.7. *Degradation in processing*

Endres *et al.* [150] carried out a fundamental study of the thermal decomposition of TPEs under thermoplastic processing conditions, more particularly of the respective kinetics, and an equation was given describing the thermal degradation of polyurethanes upon extrusion. The knowledge of these side phenomena during TPE processings is continuously improving and, for instance, Lee and White [151] observed that no by-products, more particularly carbon dioxide and water, are formed in the preparation of a polyetheramide triblock copolymer by reactive extrusion.

5. Position of TPEs among organic materials and their applications

TPEs take an intermediate position between rubbers which are soft, flexible and with elastic properties, and thermoplastics which are rigid; in fact they overlap both domains [152,153]. The respective positions of TPEs, thermoset rubbers, and plastics in terms of Shore A and D hardness are given in Figure 1 [5].

In organic and macromolecular chemistry, their preparation is attractive, regardless of the additional difficulties, compared to the synthesis of classical

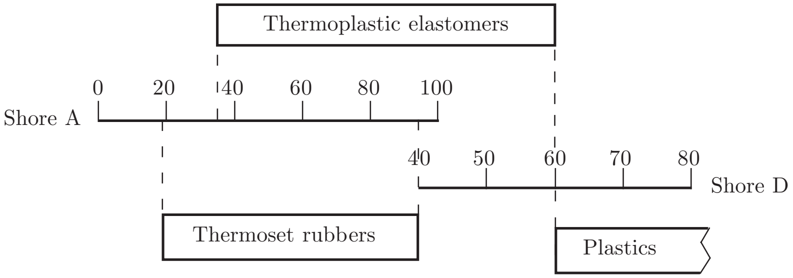

Figure 1. Respective positions of thermoset rubbers, plastics, and thermoplastic elastomers in Shore A and D hardness scales [5]

polymers, due to the incompatibility of the blocks or to the drastic control of the functionality of the precursors. On the other hand, they are processed by the same techniques and apparatuses as the thermoplastic polymers. Several authors analyzed the advantages and the drawbacks of the use of TPEs in specific fields of application. Baumann [154,155] reviewed the innovative applications of thermoplastic elastomers, showing their versatility and their advantages in design and economy.

The number of references directly related to TPE is around 7000; most of them are patents (above 95%) and many of them use the term “thermoplastic elastomer”, even though the TPE structure is far from any accepted nomenclature. This is confirmed by the very limited number of publications devoted to the control of the structure. Numerous reports describe the processing of TPEs in relation to a specific application, even though some of them treat the fundamental aspect of a specific technique. Several patents describe a processing apparatus specially designed for a definite TPE [156] or the preparation of an elastomer specifically tailored to meet some processing requirements [157]. Some very few reviews analyzed the dependences of the properties and the applications on the processing conditions [142,158].

The blends of TPE with other organic materials enjoy an important development, particularly in organized morphologies, such as multilayer laminates [159]. Their final shape is obtained by different processing techniques, such as dynamic vulcanization [160]. The preparation of the blends generates interesting studies on polymer compatibility, which calls for chemical modification in the bulk or at interfaces, as well as for thermodynamic studies and careful control [161]. The preparation of a copolymer requires a long succession of steps going from the macromers to the final product; blending is the initial operation, which requires very careful structural analyses of the mixture, before and after the copolymerization [162]. The processing of blends requires coextrusion-molding, calendering, vacuum forming, *etc.*

TPE are used for the preparation of some important synthetic fibers and elastomers, and are described in many books, reviews, and articles. The thermoplastic elastomers prepared by polycondensation and polyaddition are the subjects of several chapters of this book. However, TPE are used in numerous other applications, some of them being widely commercialized. They are briefly listed below, but numerous applications cannot be classified as belonging to a specific technical field.

Many references concern layered and sandwich structures; the different layers may cooperate to provide a desired function, particularly in mechanical properties, or each layer may be responsible for a specific function such as adhesion, electric conductivity [163], specific density, [164] or noise reduction [165].

A non-negligible number of TPEs are involved in the production of foams where they provide low density, good mechanical properties and, often, advantages in processing; some of them are vulcanized [166]. The use of supercritical fluid CO_2 in the saturation/depressurization method allowed the control of TPE foaming and the material exhibited very little hysteresis [167].

The use of TPEs in films and tapes is discussed in numerous reports. However, the latter provide essentially "recipes" of mixtures. They concern many technical fields: pressure-sensitive adhesives, medical applications, barrier properties, porous films, *etc.*, and some of them describe well defined electic properties, such as an electrostrictive system formed of a conductive polymer (polypyrrole, polyaniline, polythiophene) deposited onto opposing surfaces of a TPE film, *e.g.*, a polyurethane [168]. The same comments hold for coating and painting where TPE are mainly used in the protection of metal or alloy substrates, such as electric wires; some others impart additional functions to the protection, as is the case of optical fibers or textile fibers and different fabrics. Some few patents claim that a new TPE can be used as textile fiber with interesting properties, however these patents are almost never industrialized; on the other hand, new TPE fiber processing techniques are proposed [169].

TPEs are used as gas or liquid barriers in many applications: caps, bottles, films, separators, *etc.*, where they can be responsible for the barrier effect or for the separation. Often they represent only substrates coated with an active component but imparting, for instance, the mechanical properties; the active layer can be plasma-deposited [170]. Some very few studies analyze the influence of the TPE structure on the behavior of the membranes; Ziegel [171] showed that the rigid and flexible domains of a thermoplastic polyurethane elastomer behave in different ways in gas transport.

TPE are often associated with inorganic materials, particularly metals, glass, and fillers [172] (see also Chapter 16). The adhesion of TPE films to the mineral part often requires a coupling agent or, in the case of a metal, the surface can be modified by a physical or chemical treatment. TPE found interesting applications in the pressable TPE-based explosives for metal accelerating applications [173]. A large number of references (mostly patents) are devoted to fillers. Mark [174] reviewed and analyzed the behavior of polysiloxane elastomeric composites, including TPEs, and proposed very interesting fundamental concepts. The nanocomposites are discussed in Section 6.

The applications of TPEs in the medical, surgical, and pharmaceutical activities are rapidly developing. Many references are patents, interesting reviews were also published, but apparently the most recent reviews in this field date back to 2000 [175,176]. The TPE applications are related to very different materials, such as antibacterial materials [177,178] or the emulsions used in dermatology and cosmetology [179]. There are many applications of TPEs found in pharmacology, and in cosmetology and agriculture; some references describe both fundamental and applied scientific approaches, such as the preparation and the study of the lactide block-containing copolymers [180] or poly(3-hydroxybutyric) [181].

It would be impossible to analyze all the different commercial applications of TPEs; however it is impossible not to mention their very important role in automotive industry. Many authors reviewed this field of application [154,182]. Some particular parts of the car call for specific materials, *e.g.*, poly(ether-*b*-polyesters) are particularly appraised in air bag doors and dashboards [183] (see also Chapter 17).

6. Future trends

Several reviews speculate on the future and trends of TPEs [*e.g.*, 184,185]; a considerable part of them are published in Japanese [186,187] or Chinese [188].

This book fills an important gap, since for the first time it is entirely devoted to condensation TPEs. The following considerations place landmarks of the new chemistry in this field, rather than browsing the recent improvements of the well established TPEs. Several new techniques appeared quite recently; they are already patented, if not applied, and are very promising. This is the case of the metallo-supramolecular block copolymers [189], which result from the chelation of complexing group end-capped oligomers with different metal derivatives and the homopolymers and copolymers prepared from metal-containing macrocycles [190,191].

Yokozawa and Yokoyama [192] published important reviews and articles concerning new polycondensations, which are particularly useful in condensation TPEs; they argued that the nature of these polycondensations may be regarded as living. The process mechanism is clearly described in Figure 2 and different monomers listed in [192] were polycondensed, *e.g.*, the polycondensation of phenyl *p*-amino benzoate was initiated by the system 4-nitro-benzoate/base, leading to a polymer with a polydispersity index ranging from 1.07 to 1.34. Several block copolymers were prepared according to this technique [63].

The TPEs prepared by these new chemical methods will generate novel materials, but probably on limited production scales and with high added value. Their markets will be essentially related to medical applications, cosmetology, some specific surface treatments, *etc.*

In the more distant future, some other synthetic processes will be applied to TPEs, such as the carbon-carbon polycondensations catalyzed by metal derivatives [193,194] or the use of enzymatic catalysis in organic media [195]. The bacterial polymers are of great interest as organic materials, such as the poly(3-hydroxyalkanoates), which are potential thermoplastic elastomers. The

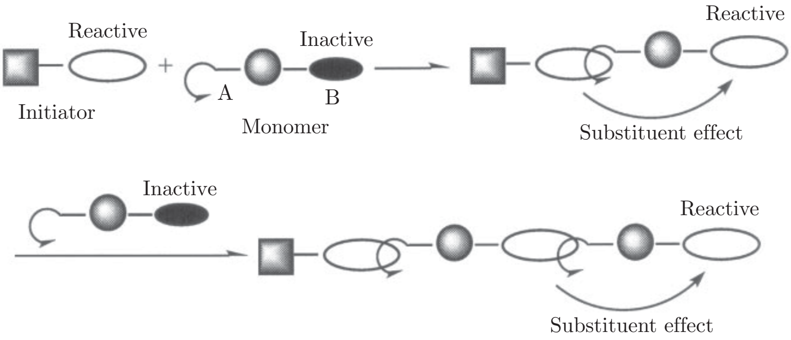

Figure 2. Effect of the substituent on the polycondensation of an A-B monomer where B becomes reactive after A has reacted with the chain [192]

respective biochemistry was reviewed by Kim and Lenz [196] and Poirier *et al.* [197–199].

The sequential reactions are rapidly developing and their contribution to the preparation of TPEs, particularly of block copolymers, will drastically increase; they were analyzed by Maréchal [39]. The sequences must not be limited to chain polymerization and polycondensation, and chemical modification will play an important role not only in grafting.

A large number of TPE syntheses depend on the existence and quality of specific functional oligomers. Their preparation and the control of their structure were reviewed by Maréchal [39] and also in Chapter 2 of this book. The oligomer chemical and structural purity, as well as functionality are responsible for the structure and morphology, hence the properties of the TPEs.

The liquid crystalline unit-containing polymers begin a timid entry in the TPE field. The liquid crystalline sequences can be part of the backbone or may be present as side chains. Nair *et al.* [200,201] carried out an abundant and very valuable work with both fundamental and applied aspects. These polymers are prepared by chain polymerization or by polycondensation and are discussed in Chapter 2. Some of them are blends and the morphology and properties of Rodrun LC3000® were the subject of two articles [202,203]. The first applications and patented products are very promising and their development should enjoy a rapid increase. This holds also for the introduction of hyperbranched and dendritic segments in block copolymers [204].

All the improvements observed in the syntheses and the advent of new products on the market result not only from the progress in organic and macromolecular chemistry, but also from the fantastic progress in structural analysis. Unfortunately, many articles and patents claim results without a deep insight in the contribution of side phenomena, whatever their nature, such as the side reactions taking place in the synthesis or the possible degradations observed during processing.

The characterization techniques will become more and more inseparable from synthesis. They were reviewed in Section 3, and the high number of techniques allow the obtaining of accurate values of the molecular masses, as well as reliable information on the nature of the blocks and that of the end-groups. Their importance will increase with the creation of new sophisticated structures and those resulting from natural products, particularly when prepared by degradation. Since the characterization of the chains remains the subject of many articles, the knowledge of their interaction and self-organization will require an increase in efficient analytical investigations; this trend is already observed in phase organization. In the same way, the morphology of the TPEs should draw increasing attention. Most of these investigations will combine theoretical and experimental studies.

Many of the improvements in TPEs and the creation of new materials result from a progressive introduction of the new achievements in chemistry, physics, and processing. However, sometimes a new technique or a new structure trigger the outburst of fundamental and applied studies and results. This is the case of the nano-technologies. Their association with TPEs is rapidly developing and several interesting reviews were published [205,206], covering an increasing number of materials: blends [207], multilayer structures [208], microemulsions [209], composites [128], stimuli-responsive polymers [210], stabilization of nanocolloidal metals [211].

The environmental protection and the recycling of TPEs are important parts of the concept and production of TPEs. Chapter 19 of this book treats these problems.

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