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Green and Sustainable Advanced Composite Materials

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Abstract
This chapter investigates the main features of biodegradable polymer including, applications of polymers, the problems of synthetic polymers, why biodegradable polymers, biodegradable polymers, copolymers. Also, the chapter gives an example of biodegradable polymers which is aliphatic polyesters include: polylactide (PLA), polycaprolactone (PCL) and polyvalerolactone (PVL). Moreover, different approaches used to synthesis polymers are presented. Depending on the manner of prepare of the polymer there are different mechanisms are discussed in this chapter.

Keywords: Green and sustainable, advanced materials, polymer

6.1 Introduction

During the past years, several topics of the search-strategic have been appeared, one of them the combination between techniques of green chemistry and nanotechnology applications. The nanomaterials are costly systems based on hazardous heavy metal such as CdS particles and Ru-compounds [1].

The green chemistry and their principles with metrics of environmental efficiencies are consider as a main approach to achieve the sustainable development that depends on three main categories: environmental, society, and economy. The principles of green chemistry are included:

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prevention, atom economy, less hazardous chemical synthesis, designing safer chemicals, safer solvents and auxiliaries, design for energy efficiency, use of renewable feedstocks, reduce derivatives, catalysis, design for degradation, real-time analysis for pollution prevention, and inherently safer chemistry for accident prevention [2, 3].

There is a good possibility of using alternative natural molecular dyes in the field of water purification. The natural dye of anthocyanin used as safe sensitizer for nanoparticles of titanium dioxide in photo-degradation process of organic pollutants in water.

The new catalyst TiO_2/anthocyanin showed effectively catalyzed the photo-degradation under solar radiation than the earlier systems previously used, while avoiding their hazardous nature as well as the possibility of enhancing their efficiency and ease to recovery from catalytic reaction by supported onto activated carbon particles, but the process need to reactivate the recovered catalyst by re-treated with fresh dye of anthocyanin due to their degradation [4].

However, some of science policy reports have mentioned that there is great opportunity and benefit by providing green nano processes by producing nanomaterials and products without pollutants harming the environment or human health at stages of managing, design, manufacturing, and application. Thus, the nanotechnology can help alleviate issues of the safe sustainable development such as environmental, human health, and safety risks and support for a sustainable environment in related with terms of energy, water, food production, raw materials, climate change, etc. [5, 6].

When the green chemistry principles are applied to nanoscience the result surely would be practicing green nanoscience that depends over each principle and methods of designing nanomaterials.

Nowadays, scientists have focused on creating a sustainable green technologies used in the manufacture of nanomaterials, as in: Nanocatalysis, Self-Assembly, used of solid state-solventless process, Non-toxic starting materials, Renewable starting materials, Safe photochemical synthesis, Aqueous processing, Bio-inspired nanoscale synthesis, Improved synthesis-fewer steps, Microwave techniques, Renewable in nanocomposites, Non-toxic starting materials, etc.[7].

It has become a trend specialist scientists to prepare biopolymers from natural sources, as in the corn plant and the roots of sugar beet where the starch is extracted from these plants and then prepare developed materials as a green nanocatalysts have a direct interest in reducing the reaction time and temperature in a safe reactors compared to common commercial processes [8].

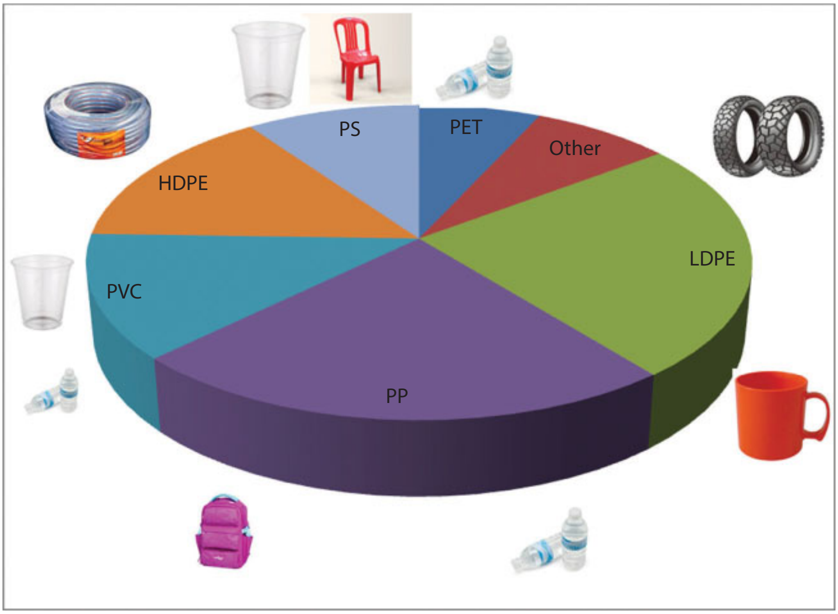


Figure 6.1 Applications of polymers.

6.2 Applications of Polymers

In spite of the huge progresses in science and technology over the last few decades, humanity is facing gradually complicated challenges in life. Most the needs of current society, for example, energy, and materials are extremely reliant on diminishing resources. The progress technology has assisted humanity to consume the main world's resources. Polymer is an example of essential material based on depleting resources [9].

Polymers are used in every part of modern life due to their applications in all aspects of human life, for example, as packaging material, agriculture, electric and other every day purposes (Figure 6.1) [10].

Subsequently, the word plastic production increase rapidly, Figure 6.2 shows that the production of plastics during the period 2004 until 2014 and this will continue to increase in future because of the spread of human population [11].

6.3 The Problems of Synthetic Polymers

The majority of polymers are based on petrochemical resources such as polyethylene and polypropylene (Figure 6.3) [12]. Such materials brought

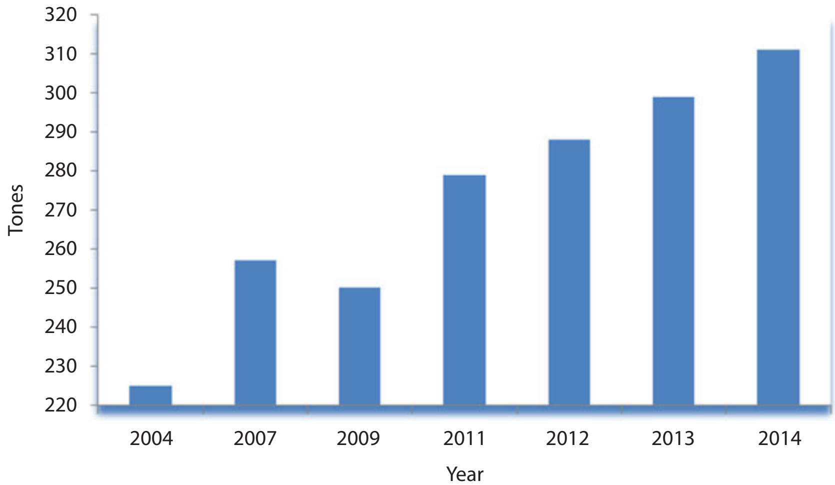


Figure 6.2 World plastic production 2004–2014 in million tones units.

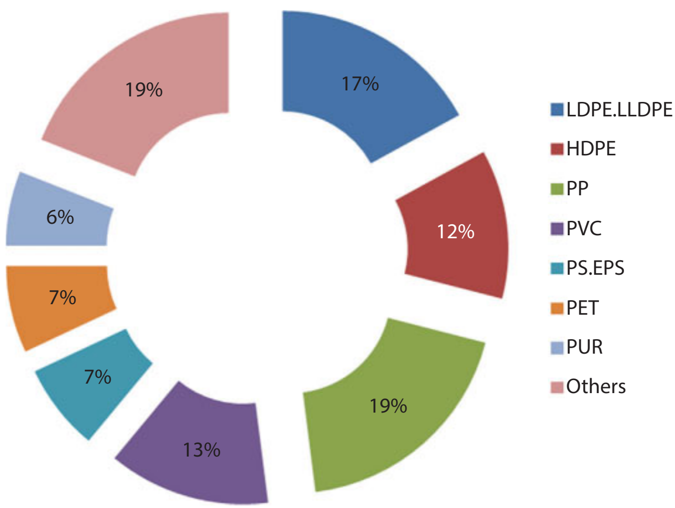


Figure 6.3 Poly (olefin)s polymers used in the worldwide.

two issues (i) they pile up in the environment because their resistance toward bacterial degradation[13], For example, (100–400) years required time to degrade plastic bags in landfill sites as compare with degradable bags can take much less time [14] (ii) they are derived from diminished resources. In addition to petroleum price fluctuation can effect on production of plastic; bearing these facts in our mind we find that the only way to maintain producing plastic, by developing new approaches to synthesize polymers derived, natural, biodegradable and renewable resources.

6.4 Why Biodegradable Polymers

At present, the challenge is to be able to produce sustainable and biodegradable resources because of environmental issues, increasing human population and human modern lifestyle. Produce biodegradable polymers are investigated by a numerical study due to their biodegradability, biocompatibility and they derived from renewable resources, moreover, there is an expectation oil will finish in the future. In addition to the usage of petroleum resources is also causal to the rise of emission of carbon dioxide into the atmosphere [15].

6.5 Biodegradable Polymers

Biodegradable polymers were date back in 1980s. Biodegradable plastics can be derived from synthetic or natural sources. Renewable resources are the main source for biodegradable polymers compared with non-degradable polymers are derived from non-renewable resources.

The environmental conditions and, the chemical structure are effect on biodegradability of polymers also it is changed by copolymerization. For example, copolymerization between cyclic esters and chitosan by using the ring opening polymerization by using different catalysts [16, 17].

6.6 Copolymers

Copolymerization of monomers such as cyclicesters copolymerization (lactide and ε-caprolactone) provides a valuable way to get new properties for polymers. For example, flexibility and thermal properties of polylactide homopolymer are less compared to that of polycaprolactone homopolymer while new copolymers between lactide and lactone has new flexibility and thermal properties can be used in different application [18]. Co-polymer can be produced by two different approaches by a block or random co-polymer. Feng *et al.*, published work they revealed that copolymerization between polylactide with polycaprolactone, capable of producing a material with more rapid polylactide degradation and polycaprolactone [19].

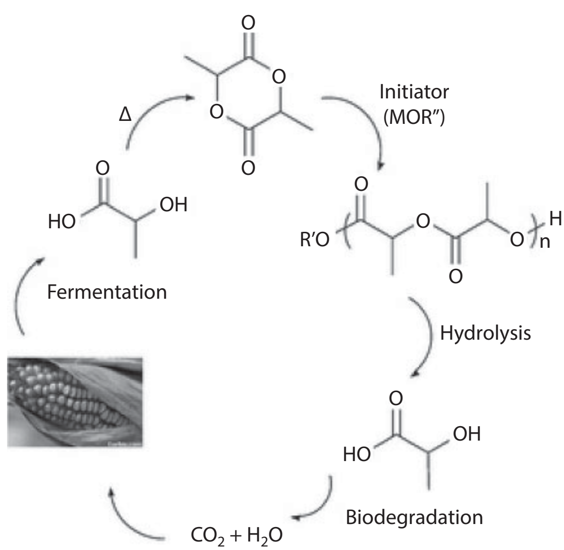
6.7 Examples of Biodegradable Polymers is Polyesters

6.7.1 Aliphatic Polyesters Polylactide PLA, Polycaprolactone PCL and Polyvalerolactone PVL

Aliphatic polyesters (polylactide, polylactones) and their co-polymers have many applications such as; medical applications as drug delivery systems (DVL) and scaffolds in tissue engineering [20]. Industry applications in production of plastic bags due to their biodegradability [21]. Regarding of availability and toxicity their monomers are derived from renewable and natural resources (Scheme 6.1), for example, lactide can be prepared from corn starch, and according to literatures review, there is no toxicity related with these polymers and therefore they are used for food packaging [22]. (Scheme 6.2) represented polymerization of lactide, ε-caprolactone and d-valerolactone.

6.7.2 Preparation of Polyesters

There are two different commercial ways are used to produce polyester. The first way is polycondensation of hydroxyl-carboxylic acid and, second way by the ring opening polymerization of their monomers



Scheme 6.1 Polylactide source, polymerization and biodegradation.

6.7.2.1 Polycondensation

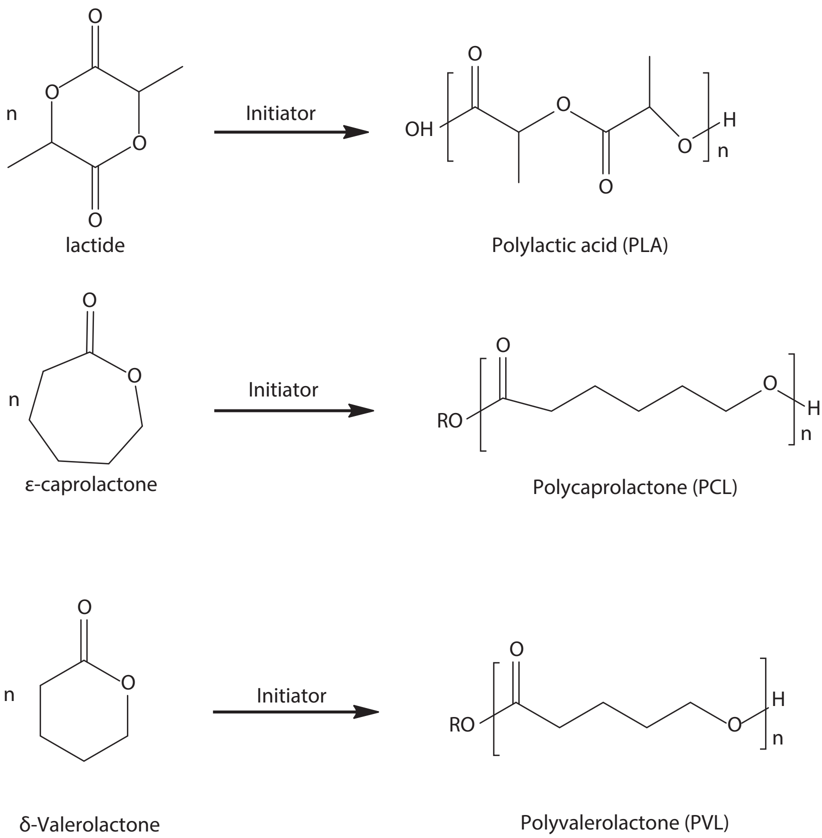
In this technique hydroxyl acid or diacidic react with diol to produce a polyester; this process includes losing water (Scheme 6.3) [23].

Recently, Braud *et al*. have reported prepare polycaprolactone oligomers without a catalyst in (6 h) at a temperature from 80 to 150°C [24].

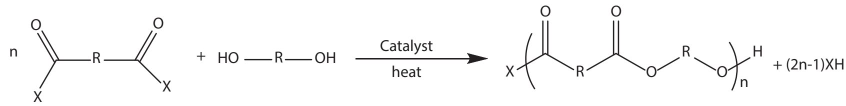
The polycondensation is less expensive; however, not easy to get high molecular weight polymers.

6.7.2.2 Ring Opening Polymerization (ROP)

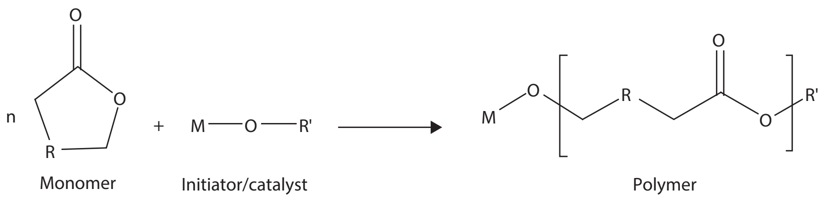
Ring opening polymerization is the typical technique with which to produce polyester from their monomers owing to the fact that control of the end group, got novel structures, and high molecular weight (Scheme 6.4) [25].



Scheme 6.2 Cyclicesters (lactide, e-caprolactone and d-valerolactone) polymerization.



Scheme 6.3 Condensation polyme.



Scheme 6.4 Polymerization of cyclic esters by ROP.

6.7.3 Mechanism of ROP

The ring opening polymerization of cyclicesters have been investigated by several study including metal alkoxides [26], carboxylates and Schiff base complexes [27] so as to achieve effective polymer synthesis.

Generally, the ring opening polymerization of cyclicesters can occur by three different mechanisms; anionic, cationic or coordination- insertion.

6.7.3.1 Cationic Ring Opening Polymerization (CROP)

Cyclicesters react with cationic catalysts to form polyesters by creating of positive charge species. Electrophilic attack is the property of the (CROP) which is then attacked by a cyclicesters (Scheme 6.5) [28].

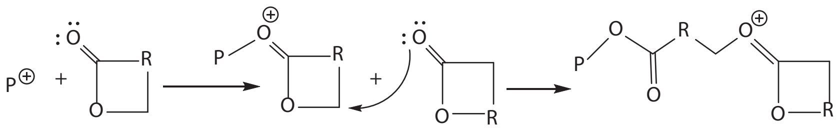
In this mechanism there are two mechanisms can happen; *active chain end* or *activated monomer*. But, using CROP to polymerize cyclicesters remains uncommon, because of side reaction may happen, difficult to control the structures and produce low molecular weight polymers [29].

6.7.3.2 Anionic Rring Opening Polymerization (AROP)

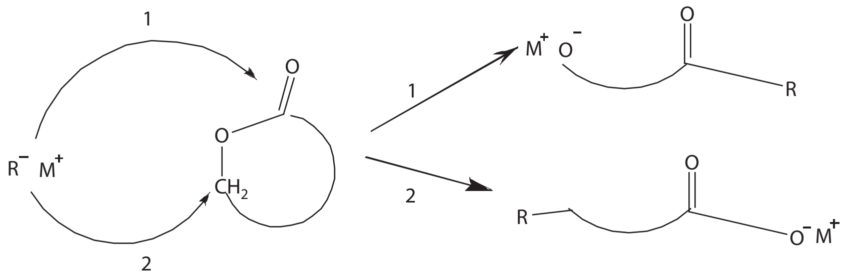
In this mechanism, the carbon atom next to the acyl-oxygen or the carbonyl carbon of the cyclicester monomer broke by the nucleophilic attack. In this case, acyl-oxygen or alkyl-oxygen cleavage will happen (Scheme 6.6) [30].

6.7.3.3 Coordination-Insertion Polymerization

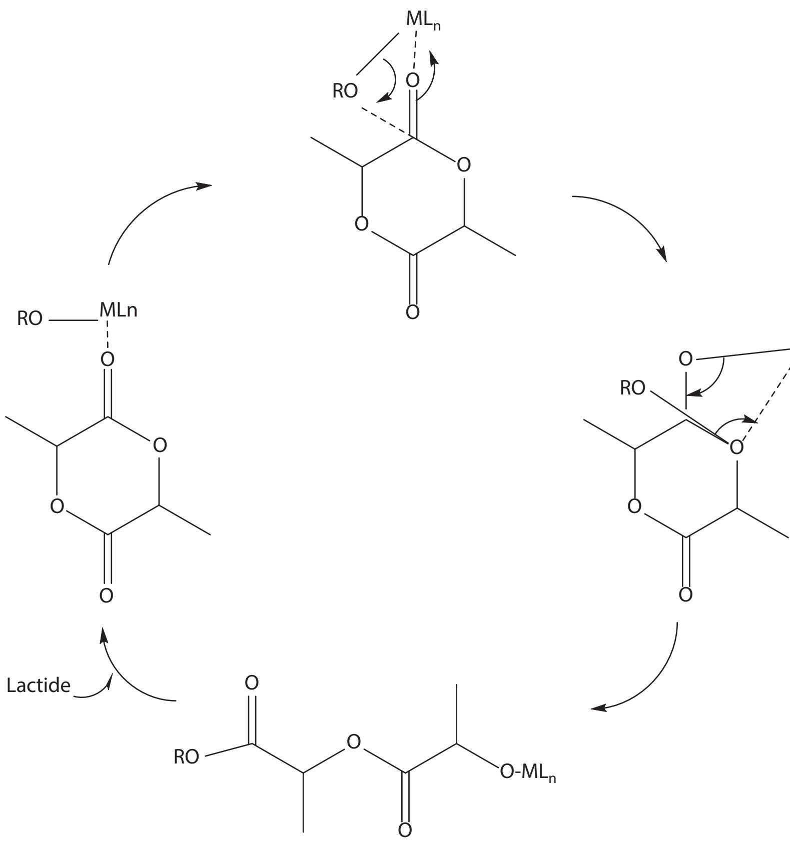
Two steps can be occurred in the coordination-insertion reaction, first: the monomer coordinate to the metal and the alkoxide will bind with the acyl



Scheme 6.5 The CROP of a cyclicester.



Scheme 6.6 The AROP of a cyclicester.



Scheme 6.7 Lactide polymerization by coordination-insertion mechanism.

carbon atom. Second: attachment of the monomer with the alkoxide group to form new metal alkoxide group then extra insertion reactions happen (Scheme 6.7) [31].

6.8 Conclusion

Sustainability of biodegradable polymer is widely studied and employed in different applications. Consequently researching of production of biodegradable polymers via a number of methods can be of much importance. This article given a review on the produce of biodegradable polymers by different ways including polycondensation and ring opening polymerization. Mechanism of ring opening polymerization including: cationic ROP, anionic ROP and coordination-insertion polymerization are discussed.

References

1. Zyoud, A., Zaatar, N., Saadeddin, I., Helal, M.H., Campet, G., Hakim, M., Park, D. and Hilal, H.S., Alternative natural dyes in water purification: Anthocyanin as TiO2-sensitizer in methyl orange photo-degradation, *Solid State Sci.*, 13, 1268, 2011.
2. Roco, M.C., Mirkin, C.A. and Hersam M.C., *J Nanopart Res*, 2011: National Science Foundation/World Technology Evaluation Center report, Springer, 2010, Boston (available on http://www.nsf.gov/nano/).
3. Dahl, J.A., Maddux, B.L.S. and Hutchison J.E., Toward greener nanosynthesis, *Chem. Rev.*, 107, 2228, 2007
4. Patet, J.M., Peng, X., Koenigsmann, C., Xu, Y., Karn, B. and Wong, S.S., Viable methodologies for the synthesis of high-quality nanostructures, *Green Chem.*, 13 (3), 482, 2011.
5. Smith, K., Al-Khalaf, A.K.H. and El-Hiti, G.A., Pattisson S. Highly regioselective di-tert-amylation of naphthalene over reusable H-mordenite zeolite, *Green Chem.*, 14, 1103, 2012.
6. Ravindra, R. and Bhat, B.R., An environmental friendly route to synthesis carbon nanofibers in bulk scale, *J. Nanoengin. Nanomanuf.*, 2, 31, 2012.
7. Reed, W. and Hutchison, W., Improved synthesis of small (d_{CORE} =1.5 nm) phosphine-stabilized nanoparticles, *J. Am. Chem. Soc.*, 122, 12890, 2000.
8. Lu, Y. and Ozcan, S., Green nanomaterials: On track for a sustainable future, *Nano Today*, 10, 417, 2015.
9. Plastic Europe, The compelling facts about plastics, 2009. online on: http://www.plasticseurope.org/pl/document/the-compelling-facts-about-plastics-2009.aspx.

10. Baytekin, B., Baytekin, H.T. and Grzybowski, B.A., Retrieving and converting energy from polymers: deployable technologies and emerging concepts, *Energy Environ. Sci.,* 6**,** 3467**,** 2013.
11. PlasticsEurope in *the Facts. PlasticsEurope*, 2015. Online on: http://www.plasticseurope.org/en
12. P. Europe in *The Compelling Facts About Plastics*, 2008. http://www.pvc.org/en/p/the-compelling-facts-about-plastics-2008.
13. Vert, M., Polymères de fermentation. Les polyacides lactiques et leurs précurseurs, les acides lactiques, *Actual Chim*., 11–12, 79, 2002.
14. Arbaoui, A. and Redshaw C., Metal catalysts for e-caprolactone polymerisation, *Polym. Chem*., 1, 801, 2010.
15. Furkan, H., Isikgor, C. and Becer, B., Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers, *Polym. Chem*., 6, 4497, 2015.
16. Willett, J.L., Mechanical properties of LDPE/granular starch composites, *J. Appl. Polym. Sci.,* 54, 1685, 1994.
17. Woo, C.J., Chun K.B.C. and Park, J.S., Ultraviolet reflective and mechanical properties of polyethylene mulching films, *Eur. Polym. J*., 37, 1227, 2001.
18. Hadjichristidis, N., Pispas, S. and Floudas, G., Block copolymers: synthetic strategies, physical properties, and applications, *JWS*., 1, 2003.
19. Song, C.X., Sun, H.F. and Feng, X.D., Microspheres of biodegradable blok copolymer for long-acting controled delivery of contraceptives, *Polym J.,* 19, 485, 1987.
20. Sinha, V.R., Bansal K., Kaushik R., Kumria, R., Trehan, A. Poly-epsilon-caprolactone microspheres and nanospheres: an overview**,** *Int. J. Pharm.,* 1, 278, 2004.
21. Kimura, Y., Molecular, structural, and material design of bio-based polymers, *J. Polym.* 41, 797, 2009.
22. Dechy-Cabaret, O., Martin-Vaca, B. and Bourissou D., Controlled ring-opening polymerization of lactide and glycolide, *Chem. Rev.,* 104, 6147, 2004.
23. Stridsberg, K.M. and Ryner, M., Albertsson, A. Controlled ring-opening polymerization: polymers withdesigned macromolecular architecture, *Springer Berlin Heidelberg, Berlin*, Heidelberg, 41, 2002.
24. Braud, C., Devarieux, R., Atlan, A., Ducos, C. and Michel, V., Capillary zone electrophoresis in normal or reverse polarity separation modes for the analysis of hydroxy acid oligomers in neutral phosphate buffer, *J. Chromatogr. B Biomed. Sci. Appl*. 706, 73, 1998.
25. Williams, C.K., Syntheses of functionalized aliphatic polyesters, *Chem. Soc. Rev.,* 36, 1573, 2007.
26. Ge, F., Dan, Y., Al-Khafaji, Y., Prior, T.J., Jiang, L., Elsegood, M.R.J. and Redshaw, R., Vanadium(V) phenolate complexes for ring opening homo- and co-polymerisation of e-caprolactone, Llactide and rac-lactide, *RSC Adv*., 6, 4792, 2016.

27. Wang, X., Zhao K., Al-Khafaji Y., Mo S., Prior T.J., Elsegood M.R.J, and Redshaw C., Organoaluminium complexes derived from anilines or Schiff bases for the ring-opening polymerization of ε-caprolactone, δ-Valerolactone and *rac*-Lactide, *Eur. J. Inorg. Chem.* 1951, 2017.
28. Rozenberg, B.A., Cationic polymerization of e-caprolactone in the presence of diols via activated monomer mechanism, *Makromol. Chem. Macromol. Symp.*, 60, 177, 1992.
29. Penczek, S., Cationic ring-opening polymerization (CROP) major mechanistic phenomena, *J. Polym. Sci. A Polym. Chem.,* 38, 1919, 2000.
30. Nuyken, O. and Pask, S., Ring-opening polymerization—an introductory review, *Polymers* 5, 361, 2013.
31. Santos, V.S. and Herres-Pawlis, S., Lactide polymerisation with complexes of neutral n-donors – new strategies for robust catalysts, *Eur. J. Inorg. Chem.*,765, 2012.