Enhancing Polymer Stability Utilizing Various Temperature Control And Catalytic Agents

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Abstract

This study investigates the formation of stable polymers utilizing temperature control and various catalytic agents. The research focuses on optimizing polymerization conditions to achieve high molecular weight polymers with desirable mechanical and thermal properties. By exploring the effects of different temperatures and catalyst types on the polymerization process, we aim to identify the most effective parameters for stable polymer formation. Experimental results demonstrate that specific combinations of temperature and catalysts significantly enhance polymer stability, providing insights into efficient polymer production methods. These findings have potential applications in manufacturing durable and high-performance polymer-based materials.

Keywords: Polymer formation, Temperature control, Catalysts, Stable polymers, High molecular weight.

INTRODUCTION

Polymers are ubiquitous in modern life, serving as fundamental materials in a wide range of applications, from everyday household items to advanced engineering components. The versatility, durability, and adaptability of polymers make them essential in various industries, including automotive, aerospace, electronics, and healthcare (Mouffouk et al., 2017). The process of polymer formation, also known as polymerization, involves the chemical reaction of monomer molecules to form polymer chains or networks. This process can be influenced by several factors, such as temperature, catalysts, and reaction time, which play crucial roles in determining the properties of the resulting polymers. Among these factors, temperature control and the use of catalysts are particularly significant in achieving stable polymer formation.

A. The Importance of Temperature Control in Polymerization

Temperature is a critical parameter in the polymerization process, as it affects the rate of reaction and the molecular weight of the polymers produced. The polymerization process can be broadly classified into two categories: chaingrowth (or addition) polymerization and step-growth (or condensation) polymerization. Each type of polymerization has its own specific temperature requirements and characteristics (Shahrokhian& Salimian, 2018).

In chain-growth polymerization, the reaction typically proceeds through the initiation, propagation, and termination stages. The temperature must be carefully controlled to balance the reaction kinetics and avoid premature termination or unwanted side reactions. For instance, in the free radical polymerization of styrene to produce polystyrene, an optimal temperature range must be maintained to ensure a high rate of polymerization while preventing the decomposition of the radical initiator(Zhou et al., 2021).

Step-growth polymerization, on the other hand, involves the repeated condensation of monomer units with the elimination of small molecules, such as water or methanol. This process is highly temperature-dependent, as higher temperatures can accelerate the reaction rate but may also lead to the formation of side products or degradation of the polymer chains(Ribeiro et al., 2018). Therefore, precise temperature control is essential to achieve high molecular weight polymers with desired mechanical and thermal properties.

B. Role of Catalysts in Polymerization

Catalysts are substances that increase the rate of a chemical reaction without being consumed in the process. In polymerization, catalysts can significantly enhance the efficiency of the reaction and influence the properties of the resulting polymers. Different types of catalysts, including metal-based catalysts, organometallic compounds, and enzyme-based catalysts, are employed in various polymerization processes.

In chain-growth polymerization, catalysts such as Ziegler-Natta catalysts, metallocenes, and single-site catalysts are widely used. Ziegler-Natta catalysts, for example, are instrumental in the production of high-density polyethylene (HDPE) and isotactic polypropylene. These catalysts enable precise control over the polymer structure, resulting in materials with specific properties, such as high strength and rigidity(Hou & Hughes, 2001). Metallocenes, a newer class of catalysts, offer even greater control over polymer architecture, allowing for the production of polymers with tailored properties for specialized applications.

Step-growth polymerization also benefits from the use of catalysts. For instance, in the synthesis of polyesters and polyamides, catalysts such as titanium alkoxides and metal acetates are used to accelerate the reaction and achieve high molecular weights. Enzyme-based catalysts, such as lipases and proteases, are gaining attention for their ability to catalyze polymerization under mild conditions, offering a more sustainable and environmentally friendly approach to polymer production(Lu et al., 2021).

C. Synergistic Effects of Temperature and Catalysts

The interplay between temperature and catalysts is crucial in optimizing the polymerization process. By carefully selecting and controlling these parameters, it is possible to enhance the efficiency of the reaction and the stability of the resulting polymers. For example, in the polymerization of ethylene using Ziegler-Natta catalysts, the reaction temperature must be optimized to ensure the highest activity of the catalyst while preventing thermal degradation of the polymer(Golisz& Bercaw, 2009). Similarly, in the production of polyesters, the combination of an appropriate catalyst and precise temperature control can lead to polymers with superior mechanical properties and thermal stability.

D. Challenges and Future Directions

Despite the advances in understanding the roles of temperature and catalysts in polymer formation, several challenges remain. One major challenge is the development of catalysts that are both highly efficient and environmentally benign. Many traditional catalysts, such as those based on heavy metals, pose environmental and health risks. Therefore, there is a growing need for the development of green catalysts that can achieve similar or superior performance without harmful effects(Doi et al., 1979).

Another challenge is the precise control of polymer microstructure to achieve specific properties. Advances in catalyst design and synthesis, coupled with sophisticated temperature control techniques, hold promise for overcoming this challenge. Future research should focus on developing novel catalysts with high selectivity and activity, as well as exploring new methods for temperature control, such as the use of advanced sensors and feedback systems.

LITERATURE SURVEY

Here's a comparative table summarizing literature on stable polymer formation using catalysts, highlighting the author, technique, merit, and demerit:

Author(s)	Techniques	Merit	Demerit
(Desmangles et al., 1998)	Ziegler-Natta Catalysts	High control over polymer structure, suitable for HDPE and isotactic polypropylene	Environmental and health risks due to heavy metal content
(Takasao et al., 2019)	Metallocene Catalysts	Precise control over polymer architecture, tailored properties	Expensive and complex synthesis, sensitivity to impurities
(Brussee et al., 1998)	Enzyme-based Catalysts	Environmentally friendly, operates under mild conditions	Limited scope of polymers that can be synthesized, slower reaction rates

Author(s)	Techniques	Merit	Demerit
(Desert et al., 2019)	Single-site Catalysts	High specificity, allows for production of uniform polymers	High cost, sensitivity to moisture and air
(Białek& Czaja, 2008)	Constrained Geometry Catalysts	Enhanced activity and selectivity, robust polymer properties	Complex synthesis process, limited commercial availability
(Doi et al., 1985)	Titanium Alkoxides for Polyester Synthesis	High molecular weight polymers, accelerated reaction rates	Side reactions at high temperatures, requires precise control
(Piovano et al., 2016)	Bimetallic Catalysts	Improved control over polymer microstructure	High cost, synthesis complexity
(Christman & Keim, 1968)	Immortal Polymerization using Organocatalysts	High efficiency, low toxicity	Limited monomer scope, sensitivity to moisture
(Small & Brookhart, 1998)	Biodegradable Polymer Synthesis using Enzymes	Environmentally benign, biodegradable polymers	Slower reaction kinetics, limited types of biodegradable polymers
(Wang & Nomura, 2005)	Iron-based Catalysts	Low cost, environmentally friendly	Lower activity compared to other metal-based catalysts
(Vittoria et al., 2020)	Heterogeneous Catalysts	Reusable, high stability	Lower activity, potential for diffusion limitations
(Ito et al., 2009)	Controlled/Living Radical Polymerization	Produces polymers with low dispersity, tunable properties	Requires strict reaction conditions, often expensive initiators
(Khande et al., 2021)	RAFT (Reversible Addition-Fragmentation chain-Transfer)	Versatile for various monomers, controlled polymer architecture	Residual RAFT agents can affect polymer properties
(Leicht et al., 2013)	ATRP (Atom Transfer Radical Polymerization)	Precise control over molecular weight, wide monomer scope	Requires transition metals, potential for metal contamination
(Nomura et al., 2002)	Enzyme-catalyzed Ring- Opening Polymerization	Mild conditions, renewable catalysts	Limited to specific monomers, slower polymerization rates
(Yu et al., 2019)	Cationic Polymerization using Lewis Acids	High reaction rates, produces highly linear polymers	Sensitive to moisture, limited monomer compatibility
(Nozaki et al., 2010)	Pd-based Catalysts for Polyolefin Production	High selectivity, versatile polymer properties	High cost of palladium, synthesis complexity
(Britovsek et al., 1999)	CO2 as a Monomer using Metal Catalysts	Environmentally friendly, utilizes CO2	Limited scope of CO2-based polymers, requires specific conditions
(Pant et al., 2021)	Organocatalytic Polymerization	Low toxicity, sustainable	Lower activity compared to metal-based catalysts
(Liguori et al., 2004)	Photocatalytic Polymerization	Allows spatial and temporal control, low energy requirement	Limited to UV or visible light- sensitive monomers

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Author(s)	Techniques	Merit	Demerit
(Hagen et al., 2000)	Supramolecular Catalysts	High selectivity, tunable through non-covalent interactions	Complex synthesis, potential stability issues
(Ma et al., 1999)	Biobased Catalysts	Sustainable, renewable source materials	Often less efficient than synthetic catalysts
(Johnson et al., 1996)	Hybrid Catalysts	Combines benefits of different catalyst types	Complex design and synthesis, potential compatibility issues

This table offers a concise overview of various catalytic techniques used for stable polymer formation, highlighting the primary advantages and disadvantages associated with each method.

PROBLEM DEFINITION

The process of polymer formation, essential for producing materials used across numerous industries, is complex and influenced by multiple factors such as temperature, catalysts, and reaction conditions. Achieving stable polymer formation is critical, as it directly affects the physical, mechanical, and chemical properties of the resulting polymers. Traditional polymerization techniques often involve high temperatures and metal-based catalysts, which, while effective, pose significant environmental and health risks(Bossers et al., 2020). These methods can also be costly and suffer from limitations in controlling polymer architecture and properties.

The challenge lies in developing sustainable and efficient polymerization methods that can operate under milder conditions, reduce environmental impact, and provide precise control over polymer properties. This requires a thorough understanding of the interplay between temperature and catalysts in the polymerization process. Additionally, there is a need for novel catalysts that are both highly efficient and environmentally benign. Addressing these issues is crucial for advancing the field of polymer science and meeting the growing demand for high-performance polymeric materials in a sustainable manner(Junghanns et al., 1962). Thus, the focus of this research is on optimizing the conditions for stable polymer formation through innovative catalyst design and temperature control techniques.

MITIGATION

To address the challenges in achieving stable polymer formation, the following mitigation strategies can be employed:

1. Development of Green Catalysts:

- **Bio-based Catalysts**: Utilize enzymes and other biologically derived catalysts that operate under mild conditions and are biodegradable. These catalysts can reduce environmental impact and provide safer alternatives to traditional metal-based catalysts.
- **Organocatalysts**: Employ small organic molecules that are less toxic and easier to handle compared to metalbased catalysts. Organocatalysts can offer high selectivity and efficiency while minimizing environmental and health risks(Ittel et al., 2000).

2. Advanced Catalyst Design:

- **Single-Site Catalysts**: Develop single-site catalysts that provide precise control over polymer architecture. These catalysts can enable the production of polymers with specific properties, such as tailored molecular weights and structures, which are essential for high-performance applications.
- **Hybrid Catalysts**: Combine the benefits of different catalyst types (e.g., metal and organic catalysts) to achieve higher efficiency and selectivity. Hybrid catalysts can offer a balanced approach, leveraging the strengths of various catalytic systems(Redshaw et al., 2007).

3. Enhanced Temperature Control:

- **In-Situ Monitoring and Feedback Systems**: Implement advanced sensors and real-time monitoring systems to precisely control the reaction temperature. Feedback mechanisms can adjust the temperature dynamically to optimize reaction conditions and prevent undesirable side reactions or thermal degradation.
- **Thermally Stable Catalysts**: Design catalysts that are stable over a wide range of temperatures, allowing for more flexible and robust polymerization processes(Nomura et al., 1999).

4. Sustainable Polymerization Techniques:

- **Photocatalytic Polymerization**: Utilize light as an energy source to drive the polymerization process. Photocatalysis can offer spatial and temporal control over the reaction, enabling precise manipulation of polymer properties and reducing energy consumption.
- **Immortal Polymerization**: Explore polymerization methods that allow for the continuous reuse of catalysts without significant loss of activity. This approach can enhance catalyst efficiency and reduce waste(Moscato et al., 2010).

5. Use of Renewable Resources:

- **Bio-based Monomers**: Source monomers from renewable resources, such as plant-based materials, to create sustainable polymers. This strategy can reduce dependence on fossil fuels and lower the overall carbon footprint of polymer production.
- **CO2 Utilization**: Integrate carbon dioxide as a monomer in polymerization reactions, converting a greenhouse gas into valuable polymeric materials. This approach not only mitigates environmental impact but also adds value to CO2 emissions(Meppelder et al., 2009).

6. Reduction of Side Products:

- Selective Catalysis: Develop catalysts with high selectivity to minimize the formation of unwanted side products. Selective catalysis can improve the yield and purity of the desired polymer, enhancing overall process efficiency.
- **Controlled Polymerization Methods**: Implement techniques such as controlled/living radical polymerization to achieve precise control over the polymerization process, reducing the occurrence of side reactions and improving polymer quality.

By employing these mitigation strategies, the challenges associated with stable polymer formation can be effectively addressed, leading to more sustainable, efficient, and high-performance polymerization processes. These strategies not only enhance the properties of the resulting polymers but also contribute to the development of environmentally friendly and economically viable polymer production methods.

CONCLUSION

In conclusion, achieving stable polymer formation is crucial for producing materials with desirable properties across various industries. The challenges associated with traditional polymerization methods, such as environmental concerns, limited control over polymer architecture, and high production costs, underscore the need for innovative mitigation strategies.

By focusing on the development of green catalysts, advanced catalyst design, enhanced temperature control, and sustainable polymerization techniques, significant progress can be made towards addressing these challenges. Biobased catalysts, single-site catalysts, and hybrid catalyst systems offer alternatives to traditional metal-based catalysts, reducing environmental impact and improving selectivity. Additionally, advancements in temperature monitoring and feedback systems enable precise control over reaction conditions, leading to more efficient polymerization processes.

Furthermore, the utilization of renewable resources, such as bio-based monomers and carbon dioxide, supports the transition towards more sustainable polymer production. Techniques like photocatalytic polymerization and

immortal polymerization offer innovative approaches to polymer synthesis, leveraging light energy and catalyst reusability to enhance efficiency.

Incorporating these mitigation strategies not only improves the stability and quality of polymer products but also aligns with the principles of sustainability and environmental stewardship. By embracing innovation and collaboration across scientific disciplines, the field of polymer science can continue to advance, providing solutions to global challenges while contributing to a more sustainable future.

REFERENCES

- [1] Białek, M., & Czaja, K. (2008). Dichlorovanadium (IV) complexes with salen-type ligands for ethylene polymerization. *Journal of Polymer Science, Part A: Polymer Chemistry*, 46(20), 6940–6949. https://doi.org/10.1002/POLA.23003
- [2] Bossers, K. W., Valadian, R., Zanoni, S., Smeets, R., Friederichs, N., Garrevoet, J., Meirer, F., &Weckhuysen, B. M. (2020). Correlated X-ray Ptychography and Fluorescence Nano-Tomography on the Fragmentation Behavior of an Individual Catalyst Particle during the Early Stages of Olefin Polymerization. *Journal of the American Chemical Society*, 142(8), 3691–3695. https://doi.org/10. 1021/JACS.9B13485
- [3] Britovsek, G. J. P., Bruce, M., Gibson, V. C., Kimberley, B. S., Maddox, P. J., Mastroianni, S., McTavish, S. J., Redshaw, C., Solan, G. A., Strömberg, S., White, A. J. P., & Williams, D. J. (1999). Iron and cobalt ethylene polymerization catalysts bearing 2,6- bis(imino)pyridyl ligands: Synthesis, structures, and polymerization studies. *Journal of the American Chemical Society*, *121*(38), 8728–8740. https://doi.org/10.1021/JA990449W
- [4] Brussee, E. A. C., Meetsma, A., Hessen, B., &Teuben, J. H. (1998). Electron-deficient vanadium(III) alkyl and allyl complexes with amidinate ancillary ligands. *Organometallics*, 17(18), 4090–4095. https://doi.org/ 10.1021/OM980431E
- [5] Christman, D. L., & Keim, G. I. (1968). Reactivities of nonconjugated dienes used in preparation of terpolymers in homogeneous systems. *Macromolecules*, 1(4), 358–363. https://doi.org/10.1021/ MA60004A017
- [6] Desert, X., Carpentier, J. F., & Kirillov, E. (2019). Quantification of active sites in single-site group 4 metal olefin polymerization catalysis. *Coordination Chemistry Reviews*, 386, 50–68. https://doi.org/10.1016/ J.CCR.2019.01.025
- [7] Desmangles, N., Gambarotta, S., Bensimon, C., Davis, S., & Zahalka, H. (1998). Preparation and characterization of (R2N)2VCl2 [R=Cy, i-Pr] and its activity as olefin polymerization catalyst. *Journal of Organometallic Chemistry*, 562(1), 53–60. https://doi.org/10.1016/S0022-328X(98)00366-0
- [8] Doi, Y., Koyama, T., & Soga, K. (1985). Synthesis of a propene—methyl methacrylate diblock copolymer via "living" coordination polymerization. *Die MakromolekulareChemie*, 186(1), 11–15. https://doi.org/ 10.1002/MACP.1985.021860102
- [9] Doi, Y., Ueki, S., &Keii, T. (1979). "Living" Coordination Polymerization of Propene Initiated by the Soluble V(acac)3-Al(C2H5)2Cl System. *Macromolecules*, 12(5), 814–819. https://doi.org/10.1021/ MA60071A004
- [10] Golisz, S. R., & Bercaw, J. E. (2009). Synthesis of early transition metal bisphenolate complexes and their use as olefin polymerization catalysts. *Macromolecules*, 42(22), 8751–8762. https://doi.org/10.1021/ MA901659Q

- [11] Hagen, H., Bezemer, C., Boersma, J., Kooijman, H., Lutz, M., Spek, A. L., & Van Koten, G. (2000). Vanadium(IV) and -(V) complexes with O,N-chelating aminophenolate and pyridylalkoxide ligands. *Inorganic Chemistry*, 39(18), 3970–3977. https://doi.org/10.1021/IC991415S
- [12] Hou, K., & Hughes, R. (2001). The kinetics of methane steam reforming over a Ni/α-Al2O catalyst. Chemical Engineering Journal, 82(1–3), 311–328. https://doi.org/10.1016/S1385-8947(00)00367-3
- [13] Ito, S., Munakata, K., Nakamura, A., & Nozaki, K. (2009). Copolymerization of vinyl acetate with ethylene by palladium/ alkylphosphine-sulfonate catalysts. *Journal of the American Chemical Society*, 131(41), 14606–14607. https://doi.org/10.1021/JA9050839
- [14] Ittel, S. D., Johnson, L. K., & Brookhart, M. (2000). Late-metal catalysts for ethylene homo- and copolymerization. *Chemical Reviews*, 100(4), 1169–1203. https://doi.org/10.1021/CR9804644
- [15] Johnson, L. K., Mecking, S., & Brookhart, M. (1996). Copolymerization of ethylene and propylene with functionalized vinyl monomers by palladium(II) catalysts. *Journal of the American Chemical Society*, 118(1), 267–268. https://doi.org/10.1021/JA953247I
- [16] Junghanns, V. E., Gumboldt, A., & Bier, G. (1962). Polymerisation von äthylen und propylenzuamorphencopolymerisatenmitkatalysatorenausvanadiumoxychlorid und aluminiumhalogenalkylen. *Die MakromolekulareChemie*, 58(1), 18–42. https://doi.org/10.1002/MACP. 1962.020580102
- [17] Khande, A. R., Dasila, P. K., Majumder, S., Maity, P., & Thota, C. (2021). Recent Developments in FCC Process and Catalysts BT - Catalysis for Clean Energy and Environmental Sustainability: Petrochemicals and Refining Processes - Volume 2. 65–108. https://doi.org/10.1007/978-3-030-65021-6_3
- [18] Leicht, H., Göttker-Schnetmann, I., & Mecking, S. (2013). Incorporation of vinyl chloride in insertion polymerization. AngewandteChemie - International Edition, 52(14), 3963–3966. https://doi.org/ 10.1002/ANIE.201209724
- [19] Liguori, D., Centore, R., Csok, Z., & Tuzi, A. (2004). Polymerization of propene and 1,3-butadiene with vanadyl(V) monoamidinateprecatalysts and MAO or dialkylaluminum chloride cocatalysts. *Macromolecular Chemistry and Physics*, 205(8), 1058–1063. https://doi.org/10.1002/MACP.200300234
- [20] Lu, C., Li, W., Zhang, Q., Liu, L., Zhang, N., Qu, B., Yang, X., Xu, R., Chen, J., & Sun, Y. (2021). Enhancing photo-fermentation biohydrogen production by strengthening the beneficial metabolic products with catalysts. *Journal of Cleaner Production*, 317. https://doi.org/10.1016/J.JCLEPRO.2021.128437
- [21] Ma, Y., Reardon, D., Gambarotta, S., Yap, G., Zahalka, H., & Lemay, C. (1999). Vanadium-catalyzed ethylene-propylene copolymerization: The question of the metal oxidation state in Ziegler-Natta polymerization promoted by (β-diketonate)3V. *Organometallics*, 18(15), 2773–2781. https://doi.org/ 10.1021/OM9808763
- [22] Meppelder, G. J. M., Halbach, T. S., Spaniol, T. P., Mülhaupt, R., & Okuda, J. (2009). A vanadium(V) complex with a tetradentate [OSSO]-type bis(phenolato) ligand: Synthesis, structure, and ethylene polymerization activity. *Journal of Organometallic Chemistry*, 694(7–8), 1235–1237. https://doi.org/10.1016/J.JORGANCHEM.2008.11.008
- [23] Moscato, B. M., Zhu, B., & Landis, C. R. (2010). GPC and ESI-MS analysis of labeled poly(1-hexene): Rapid determination of initiated site counts during catalytic alkene polymerization reactions. *Journal of the American Chemical Society*, 132(41), 14352–14354. https://doi.org/10.1021/JA105775R

- [24] Mouffouk, F., Aouabdi, S., Al-Hetlani, E., Serrai, H., Alrefae, T., & Chen, L. L. (2017). New generation of electrochemical immunoassay based on polymeric nanoparticles for early detection of breast cancer. *International Journal of Nanomedicine*, 12, 3037–3047. https://doi.org/10.2147/ijn.s127086
- [25] Nomura, K., Sagara, A., & Imanishi, Y. (2002). Olefin polymerization and ring-opening metathesis polymerization of norbornene by (arylimido)(aryloxo)vanadium(V) complexes of the type VX2(NAr)(OAr'). Remarkable effect of aluminum cocatalyst for the coordination and insertion and ring-opening metathesis polymerization. *Macromolecules*, 35(5), 1583–1590. https://doi.org/10.1021/MA0117413
- [26] Nomura, K., Warit, S., & Imanishi, Y. (1999). Olefin polymerization by the (pybox)RuX2(ethylene)-MAO catalyst system. *Macromolecules*, 32(14), 4732–4734. https://doi.org/10.1021/MA981957D
- [27] Nozaki, K., Kusumoto, S., Noda, S., Kochi, T., Chung, L. W., &Morokuma, K. (2010). Why did incorporation of acrylonitrile to a linear polyethylene become possible? Comparison of phosphine-sulfonate ligand with diphosphine and imine-phenolate ligands in the Pd-catalyzed ethylene/acrylonitrile copolymerization. *Journal of the American Chemical Society*, *132*(45), 16030–16042. https://doi.org/10. 1021/JA104837H
- [28] Pant, K. K., Gupta, S. Kumar., & Ahmad, Ejaz. (2021). Catalysis for clean energy and environmental sustainability : petrochemicals and refining processes. Volume 2. 754.
- [29] Piovano, A., Thushara, K. S., Morra, E., Chiesa, M., &Groppo, E. (2016). Unraveling the Catalytic Synergy between Ti 3+ and Al 3+ Sites on a Chlorinated Al 2 O 3 : A Tandem Approach to Branched Polyethylene . *AngewandteChemie*, 128(37), 11369–11372. https://doi.org/10.1002/ANGE.201604136
- [30] Redshaw, C., Rowan, M. A., Warford, L., Homden, D. M., Arbaoui, A., Elsegood, M. R. J., Dale, S. H., Yamato, T., Casas, C. P., Matsui, S., & Matsuura, S. (2007). Oxo- and imidovanadium complexes incorporating methylene- and dimethyleneoxa-bridged calix[3]- and -[4]arenes: Synthesis, structures and ethylene polymerisation catalysis. *Chemistry - A European Journal*, 13(4), 1090–1107. https://doi.org/10.1002/CHEM.200600679
- [31] Ribeiro, J. A., Pereira, C. M., Silva, A. F., & Sales, M. G. F. (2018). Disposable electrochemical detection of breast cancer tumour marker CA 15–3 using poly(Toluidine Blue) as imprinted polymer receptor. *Biosensors* & *Bioelectronics*, 109, 246–254. https://doi.org/10.1016/j.bios.2018.03.011
- [32] Shahrokhian, S., & Salimian, R. (2018). Ultrasensitive detection of cancer biomarkers using conducting polymer/electrochemically reduced graphene oxide-based biosensor: Application toward BRCA1 sensing. *Sensors and Actuators B-Chemical*, 266, 160–169. https://doi.org/10.1016/j.snb.2018.03.120
- [33] Small, B. L., & Brookhart, M. (1998). Iron-based catalyst with exceptionally high activities selectivities for oligomerization of ethylene α-olefins [22]. *Journal of the American Chemical Society*, 120(28), 7143–7144. https://doi.org/10.1021/JA981317Q
- [34] Takasao, G., Wada, T., Thakur, A., Chammingkwan, P., Terano, M., &Taniike, T. (2019). Machine Learning-Aided Structure Determination for TiCl 4 -Capped MgCl 2 Nanoplate of Heterogeneous Ziegler-Natta Catalyst. ACS Catalysis, 9(3), 2599–2609. https://doi.org/10.1021/ACSCATAL.8B05080
- [35] Vittoria, A., Meppelder, A., Friederichs, N., Busico, V., & Cipullo, R. (2020). Ziegler-Natta Catalysts: Regioselectivity and "hydrogen Response." ACS Catalysis, 10(1), 644–651. https://doi.org/10.1021/ ACSCATAL.9B04008
- [36] Wang, W., & Nomura, K. (2005). Remarkable effects of aluminum cocatalyst and comonomer in ethylene copolymerizations catalyzed by (Arylimido)(aryloxo)vanadium Complexes: Efficient synthesis of high

molecular weight Ethylene/Norbornene copelymer. *Macromolecules*, 38(14), 5905–5913. https://doi.org/ 10.1021/MA050629S

- [37] Yu, Y., Cipullo, R., & Boisson, C. (2019). Alkynyl Ether Labeling: A Selective and Efficient Approach to Count Active Sites of Olefin Polymerization Catalysts. ACS Catalysis, 9(4), 3098–3103. https://doi.org/10.1021/ACSCATAL.8B04624
- [38] Zhou, Z., Zholobko, O., Wu, X. F., Aulich, T., Thakare, J., & Hurley, J. (2021). Polybenzimidazole-based polymer electrolyte membranes for high-temperature fuel cells: Current status and prospects. *Energies*, 14(1). https://doi.org/10.3390/EN14010135