

Synthesis and characterization of novel poly(α -methyl β -alanine- γ -lactone)s through hydrogen-transfer and ring-opening polymerization

Efkan ÇATIKER*,¹ Songül KIRLAK,¹ Mehmet ATAKEY,² and Bekir SALİH²

¹Ordu University, Faculty of Science & Literature, Department of Chemistry, 52200, Ordu, Turkey

²Hacettepe University, Faculty of Science, Department of Chemistry, 06800, Ankara, Turkey

Abstract. A series of novel poly(α -methyl β -alanine- γ -lactone)s were prepared by a combination of hydrogen-transfer polymerization (HTP) of methacrylamide (MAM) and anionic ring-opening polymerization (AROP) of β -propiolactone (BPL), β -butyrolactone (BBL), and δ -valerolactone (DVL). For this purpose, poly(α -methyl β -alanine) (PmBA) having a living anionic end-group for a further extension was obtained via HTP of MAM. The anionic end-group on PmBA chains were used as initiation sites for AROP of BPL, BBL, and DVL. Fourier Transform Infrared Spectroscopy (FTIR) and Proton Nuclear Magnetic Resonance Spectroscopy (¹H-NMR) confirmed the existence of both ester and α -methyl β -alanine (mBA) units in the final products. MALDI-MS analysis revealed that the poly(α -methyl β -alanine- γ -lactone)s with average molar masses of several thousand g·mol⁻¹ were obtained. DSC and TGA thermograms of each copolymer showed that the copolymers comprised the mBA and the corresponding ester units.

Keywords: AB-type block copolymers; poly(amide-ester); hydrogen-transfer polymerization; ring-opening polymerization.

1. Introduction

Block copolymer is a particular class of polymer in which blocks of different repeating units are placed along the polymer chain. Block copolymers have advantages over homopolymers or other types of copolymers in that different functionalities for different tasks can be built into different blocks. Main application of block copolymers is based on the design of advanced materials such as thermoplastic elastomers [1], drug delivery matrices [2], porous materials [3], compatibilizers [4], adhesives [5], and nanopatterned materials by lithography [6]. Developing new synthetic strategies yields well-defined macromolecular architectures that can be prepared [7]. One of the main approaches to obtain linear block copolymers is to obtain a macroinitiator and its extension using a different monomer if its end-group is a polymerization initiating moiety. The macroinitiator can be synthesized via polymerization reactions such as free radical [8], anionic [9], cationic [10], or ring-opening [11].

Base-catalyzed hydrogen transfer polymerization (HTP) is a well-known route for the synthesis of nylon-3 (poly- β -alanine) from acrylamide [12]. However, some studies have been also reported for methacrylamide [13–21]. Yamaguchi and Minoura [13] have reported that optically active poly(α -methyl β -alanine) could be obtained by using optically active alcoholates as an initiator of HTP. Nakayama et al. [16] reported that both HTP and vinyl polymerizations occur in the polymerization of methacrylamide with basic initiators. HTP of methacrylamide with basic initiators proceeded to a high yield of poly(α -methyl β -alanine) by Okamura et al. [21]. Recently, many studies emerged to

demonstrate that poly- β -alanine derivatives and copolymers are potential biomaterials [22–25].

In numerous studies, poly(hydroxyalkanoates)'s mentioned as biodegradable and biocompatible materials [26–28]. These polymers can be readily synthesized by AROP of the corresponding lactone [29, 30]. Considering the given literature summary above, the copolymers containing α -methyl β -alanine and readily biodegradable/biocompatible units (3-hydroxy propionate, 3-hydroxy butyrate, and 5-hydroxy valerate) may also behave as biomaterials in various fields. Within this scope, synthesis of novel poly(ester amide)s was planned via HTP and AROP mechanism, where methacrylamide (MAM) and a series of lactones would be used as monomers.

2. Experimental

2.1. Materials

Methacrylamide (Fluka 99%), β -propiolactone (BPL, Acros Organics 99%), β -butyrolactone (BBL, Sigma-Aldrich 98%), and δ -valerolactone (DVL, Acros Organics 99%) to be used as a monomer in the synthesis studies were obtained commercially and used without purification. HTP was carried out in an argon atmosphere using sodium tert-butoxide (*t*-BuONa, Sigma-Aldrich 97%) as initiator and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, Acros Organics 98%) as a radical polymerization inhibitor. The concentrations of the monomers, initiator, and inhibitor used were summarized in Table 1.

2.2. Synthesis of polymers

MAM, *t*-BuONa, and TEMPO indicated in Table 1 were placed in 10 mL-salinated round bottom flasks. The

*Corresponding author. E-mail address: ecatiker@gmail.com (Efkan Çatiker)

flasks capped with rubber septum were placed in an oil bath and purged with argon. The temperature was adjusted to 105 °C. The polymerization was complete in about 3 hours, and the reaction medium completely solidified. After the product [living poly(α -methyl β -alanine)] was allowed to cool to room temperature, the rubber septum was drilled by a steel needle to scrape the solid product into small pieces. The lactones were then added to each flask using a glass syringe. Stirring was continued at room temperature, first with the aid of a vortex and then with a magnetic stirrer until the product solidified utterly. Excess acetone slightly acidified with acetic acid was added and stirred using a magnetic stirrer until a suspension had occurred. Finally, the copolymer was separated by vacuum filtration and dried in a vacuum oven for characterization. The yields given in Table 1 were determined gravimetrically.

Table 1. Reaction parameters applied in copolymer synthesis.

Initiator: *t*-BuONa ($[I]=[M]_0/30$), inhibitor: TEMPO ($[M]_0/1000$), MAm ($[M]_0=0.01$ mol) feed rate: 20%, temperature: 105 °C (first stage) and room temperature (second stage)

Sample code	Monomer feed rates mol %	Monomer feed rates mol %	Copolymer yield (%)
P13	20 MAm	80 BPL	92.3
B13	20 MAm	80 BBL	47.8
D13	20 MAm	80 DVL	23.5

2.3. Polymers characterization

FTIR spectra were acquired using Shimadzu IRAffinity 1 spectrometer using the ATR technique with 32 scans in the range of 4000-600 cm^{-1} . $^1\text{H-NMR}$ spectra of the obtained copolymers were recorded using Bruker AVANCE III 400 MHz NMR Spectrometer. Thermal transitions in a nitrogen atmosphere were determined using TA Instruments DSC Q2000 by a heating rate of 10 °C/min. TGA thermograms of the copolymers were acquired by using TA Instruments SDT Q600. Samples were heated ambient temperature to 425 °C at a 10 °C/min heating rate under nitrogen flux. Differential thermogravimetry (DTG) curves were drawn to understand the degradation behavior better. MALDI-MS analyzes were performed with Bruker Rapidflex MALDI-ToF/ToF mass spectrometer (Bruker Daltonics, Bremen, Germany). Data were obtained with positive ion mode. A solution of 2,5-dihydroxybenzoic acid (DHB) (20 mg/mL, 1:1, ACN: THF) containing 1% by volume of formic acid was used as a matrix.

3. Results and discussion

3.1. Synthesis of poly(α -methyl β -alanine-*b*-lactone)s

MAm and the three lactones (BPL, BBL, and DVL) as comonomers were used to synthesize a series of novel poly(α -methyl β -alanine-*b*-lactone)s coded as P13, B13, and D13, respectively. The copolymers were synthesized via sequentially HTP and AROP methods. Firstly, HTP of methacrylamide (Figure 1) by *t*-BuONa initiator at 105 °C was performed as reported in the literature [31]. At the end of the polymerization, the

chain-ends were assumed to be active (viable), i.e., the chain extension can continue with the addition of any monomer capable of polymerizing through an anionic mechanism. In other words, the product was assumed to be living PmBA oligomers.

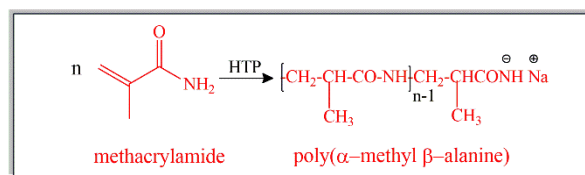


Figure 1. Reaction outline to obtain living PmBA oligomer

Then, the chain extension of the living PmBA oligomers was achieved by adding predetermined amounts of lactones, as outlined in Figure 2. The yields in Table 1 were calculated considering the masses of the acetone-insoluble fractions of the copolymers and the total masses of the monomers. The relatively low copolymer yields were attributed to the homo-polyesters removed by washing with acetone during the isolation process. As well-known, the homo-polyesters occur by the chain transfer to monomer [32] during the AROP. As will be discussed later, the chain transfer to the monomer causes low degrees of chain extension, especially in the D13 sample.

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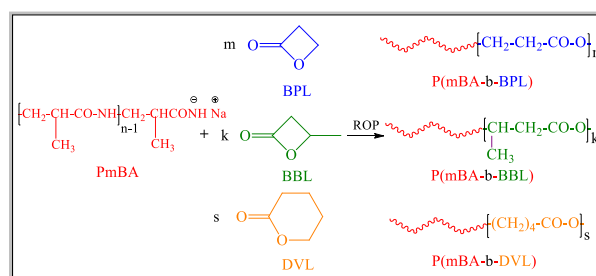


Figure 2. Reaction pathways to obtain poly(α -methyl β -alanine-*b*-lactone)s

3.2. Characterization of poly(α -methyl β -alanine-*b*-lactone)s

The FTIR spectra of each isolated copolymer (acetone-insoluble fraction) given in Figure 3 were recorded to examine the availabilities of the amide and the ester units. All the spectra have the stretching bands of the ester carbonyls and the secondary amide carbonyl at about 1730 cm^{-1} and 1640 cm^{-1} , respectively. As well-known, the band at about 3290 cm^{-1} belongs to the N-H stretching of the secondary amide. Comparing the relative intensities of the carbonyl bands of the ester and

the amide units, the success of the chain extensions may be estimated as in the order of BPL, BBL, DVL.

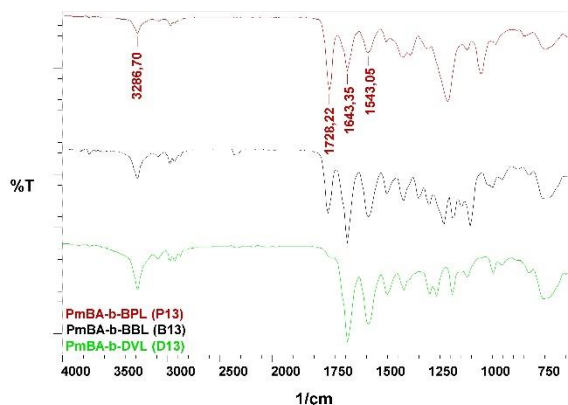


Figure 3. FTIR spectra of P13, B13, and D13 copolymers

$^1\text{H-NMR}$ spectra of the P13, B13, and D13 were given in Figure 4. The peaks observed at 1.38, 3.10, 3.69, and 8.15 ppm for the P13 sample in Figure 4 (A) belong to the protons of CH_3 , CH , CH_2 , and NH in mBA units, respectively. As quickly shown, the four signals

are common for the three spectra, as expected. In the spectrum of P13, the peaks observed with equal intensity at 2.97 and 4.67 ppm are CO-CH_2 and O-CH_2 protons in BPL units, respectively. The relative intensities of the peaks belonging to the ester and amide units seem to be consistent with the relative intensities shown in the FTIR spectrum of the P13 copolymer.

$^1\text{H-NMR}$ spectrum in Figure 4 (B) has the additional signals at 1.43, 3.09, and 5.51 ppm attributed to the CH_3 , CH_2 , and CH protons in BBL units, respectively. Considering the intensities of CH_3 protons in both units, one can conclude that units of BBL are slightly lower than those of mBA in the copolymer sample B13. The $^1\text{H-NMR}$ spectrum of D13 samples in Figure 4 (C) has three trace peaks at 1.83, 2.57, and 4.30 ppm belonging to the CH_2 protons in the DVL unit. The intensity of the peak at 1.83 ppm is twice since it belongs to the beta and gamma methylene. The other peaks with equal intensity are methylene protons at alpha and delta positions. The relative intensities of the signals for DVL and mBA units show that the chain extension with DVL remains extremely limited.

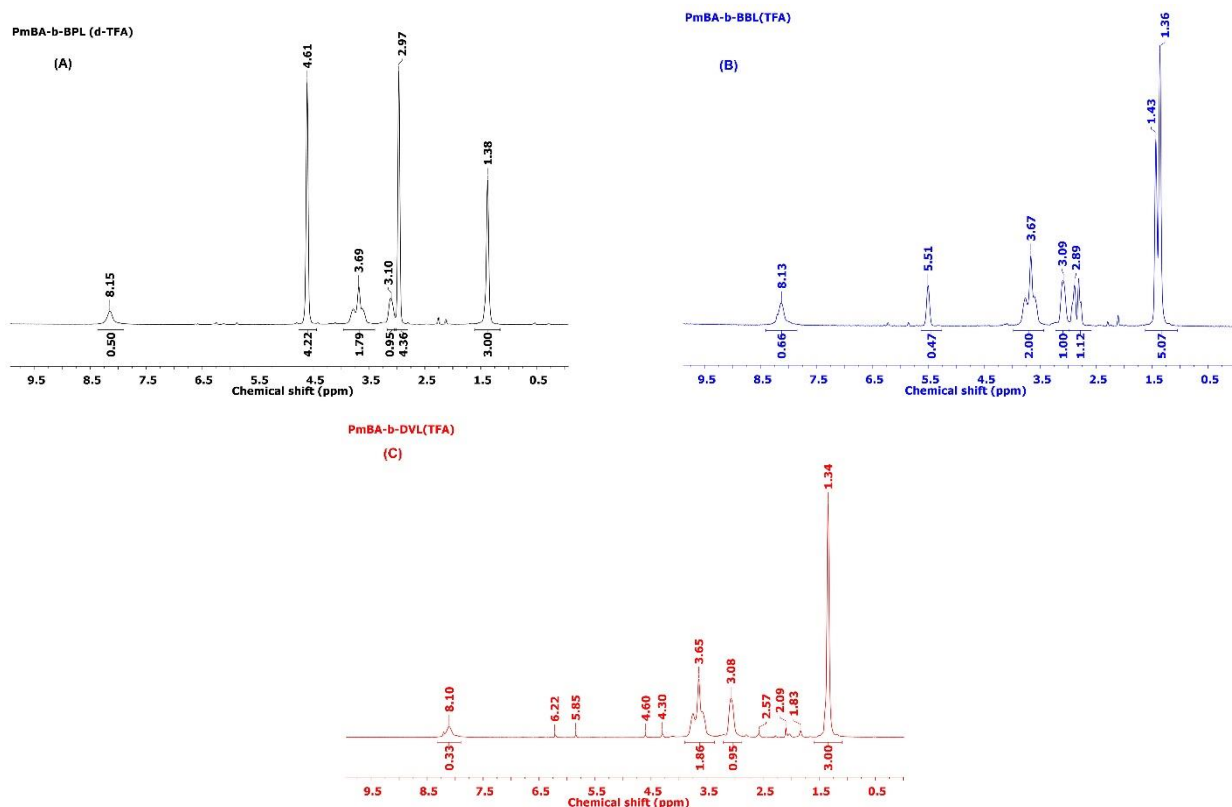


Figure 4. $^1\text{H-NMR}$ spectra of P13 (A), B13 (B), D13 (C) copolymer samples

This result is due to polyesters being removed as homopolymers during washing off the final product with acetone. It is also the main reason for the low yields, as given in Table 1. The formation of polyester homopolymer is the direct result of chain transfer to the monomer [29, 33] and possibly transesterification [34, 35] reactions. The undesirable side reactions can also be regarded as the most crucial reason for the failure of the copolymer to be synthesized at the expected molar masses.

DSC thermograms of all the copolymer samples in Figure 5 were recorded to determine the glass and the

melting transitions of the amide and the ester blocks in the copolymers. The values of observed transitions are outlined in Table 3. There are limited studies on the thermal analyses of both the PmBA [36, 37] and the homo-polyesters [37–40] under consideration. The DSC curve for the P13 sample has two endothermic bands centered at about 75 and 123 °C attributed to melting phenomena for the ester and the amide blocks, respectively. Considering the literature knowledge [38] the baseline shift at -15.50 °C may easily be attributed to the glass transition of the ester (3-hydroxy propionate) block.

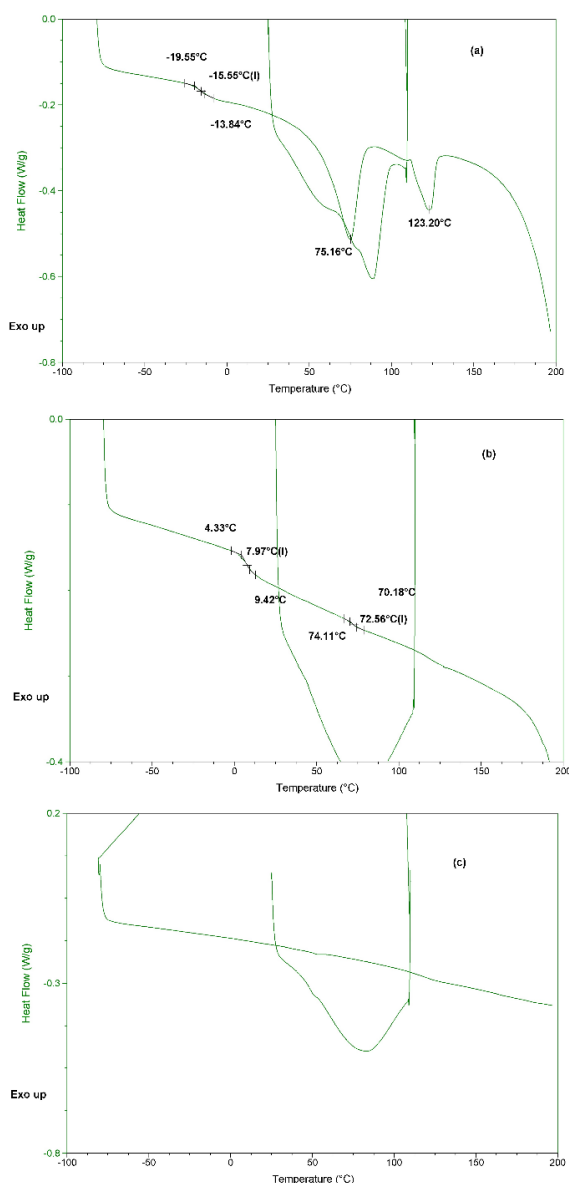
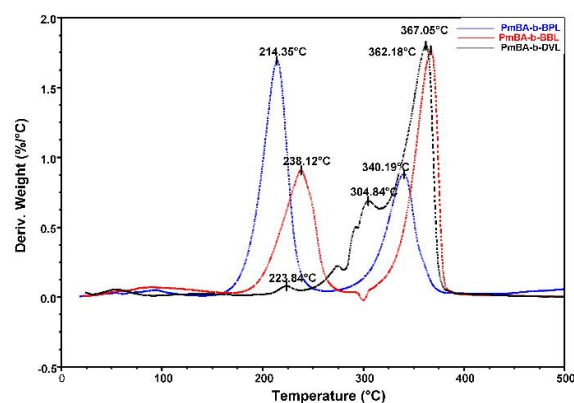

Figure 5. DSC curves of the P13, B13, and D13 copolymers

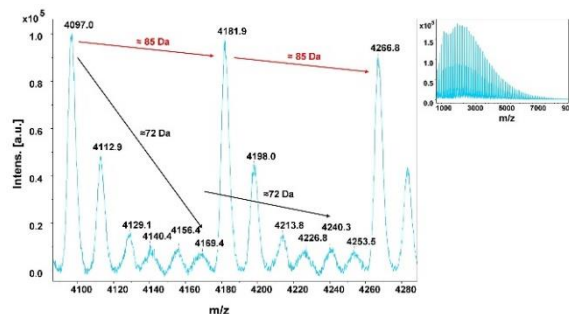
Table 3. Thermal transition temperatures observed in DSC and TGA thermograms of all copolymers (T_g : glass transition temperature, T_m : melting temperature, T_d : decomposition temperature)

Code	T_g (°C)	T_g (°C)	T_m (°C)	T_{d1} (°C)	T_{d2} (°C)
P13	-15.5	-	76.16	214.35	340.19
B13	7.97	72.51	-	238.12	367.05
D13	-	-	-	223,84	362.18

TGA thermograms of P13, B13, and D13 were recorded to determine the thermal stability of each copolymer. DTG curves in Figure 6 revealed that the copolymers decomposed in two steps. As recently has been reported for the poly(ester-ether) block copolymers [41], the ester and mBA units in the copolymers have decomposed, respectively. Thermal decomposition temperatures (T_d) of each component in the copolymers were observed separately for the ester (T_{d1}) and mBA (T_{d2}) units. The relative mass-loss values of the ester and amide units for each copolymer seem to be consistent with the observations in the FTIR and the NMR sections.


Figure 6. DTG curves of the copolymers

Although FTIR, $^1\text{H-NMR}$, DSC, and TGA methods revealed that the final products contained aliphatic esters and mBA units, the MALDI mass spectrum of the P13 was examined to show clearly that the mBA and the 3-hydroxy propionate units were in the same chains, namely, covalently bonded. The MALDI mass spectrum of the P13 sample given in Figure 7 was examined in detail to reveal the fact.


Figure 7. Expanded MALDI mass spectrum of P13 copolymer

Figures 7 include an extended version of a particular spectrum region with the broad spectrum provided on the right. The repeating units (mBA/BPL) of the copolymers P13 have masses of 85/72 Da. The mass differences between the signals corresponding to both BPL and mBA masses were observed. For example, the signals 4097.0 Da and 4181.9 Da indicate the difference of 85 Da mBA units, 4097.0 Da, and 4169.4 Da, indicating the difference of BPL, 72 Da. This result shows two different units (mBA and BPL) in the same chain. The approach is well-known in literature [42–44] to prove the formation of block copolymers.

4. Conclusions

It can be concluded that poly(α -methyl β -alanine- β -lactone)s have been synthesized successfully considering the results of the spectroscopic and thermal analyses. Although the synthesis of the block copolymers via sequential living polymerization of two monomers is typical, it is novel to obtain them by sequentially applying HTP and AROP reactions. The three types of poly(ester-amide) containing the three different ester units (β -butyrolactone, β -propiolactone, and δ -valerolactone) may be regarded as potential novel biomaterials considering the previous reports on the components of the copolymers. However, the biggest

obstacle for application is limited molar masses. Different polymerization methods (ring-opening copolymerization of β -lactam and lactones, solution polymerization at low temperature in a moisture-free medium), and different organometallic catalysts systems can enhance the molar mass. Thus, not only increasing the mole mass, but also random and sequential poly (ester-amide)s can be synthesized.

Conflict of interest

Authors declare no conflict of interest.

References

- [1]. B. Dufour, K. Koynov, T. Pakula, K. Matyjaszewski, PBA–PMMA 3-Arm Star Block Copolymer Thermoplastic Elastomers, *Macromolecular Chemistry Physics* 209 (2008) 1686–1693. Doi: 10.1002/macp.200800151
- [2]. G. Gaucher, M.H. Dufresne, V.P. Sant, N. Kang, D. Maysinger, J.C. Leroux, Block copolymer micelles: preparation, characterization and application in drug delivery, *Journal Control Release* 109 (2005) 169–188. Doi: 10.1016/j.jconrel.2005.09.034
- [3]. M.A. Hillmyer, Nanoporous Materials from Block Copolymer Precursors BT - Block Copolymers II. In: Abetz V (ed). Springer Berlin Heidelberg, Berlin, Heidelberg, (2005) pp. 137–181
- [4]. P. Samanta, R. Srivastava, B. Nandan, (2018) Block copolymer compatibilization driven frustrated crystallization in electrospun nanofibers of polystyrene/poly(ethylene oxide) blends. *Royal Society Chemistry Advances* 8 (2018) 17989–18007. Doi: 10.1039/C8RA02391C
- [5]. A.A. Scherbina, A.E. Chalykh, Adhesive Compositions Based on Styrene–Isoprene–Styrene Three-Block Copolymer with Different Modifiers. *Polymer Science, Serie D* 11 (2018) 140–146. Doi: 10.1134/S1995421218020168
- [6]. M.P. Stoykovich, P.F. Nealey, Block copolymers and conventional lithography, *Materials Today* 9 (2006) 20–29. Doi: 10.1016/S1369-7021(06)71619-4
- [7]. D. Le, T.N.T. Phan, L. Autissier, L. Charles, D. Gigmes, A well-defined block copolymer synthesis via living cationic polymerization and nitroxide-mediated polymerization using carboxylic acid-based alkoxyamines as a dual initiator, *Polymer Chemistry* 7 (2016) 1659–1667. Doi: 10.1039/C5PY01934F
- [8]. X. Tian, J. Ding, B. Zhang, F. Qui, X. Zhuang, Y. Chen, Recent Advances in RAFT Polymerization: Novel Initiation Mechanisms and Optoelectronic Applications, *Polymers (Basel)* 10 (2018) 318. Doi: 10.3390/polym10030318
- [9]. E. Çatiker, T. Öztürk, M. Atakay, B. Salih, Synthesis and characterization of novel ABA type poly(Ester-ether) triblock copolymers. *Journal of Polymer Research* 26 (2019) 123–132. Doi: 10.1007/s10965-019-1778-5
- [10]. K. Adachi, Y. Tsukahara, Macroinitiator and Macromonomer: Preparation and Application BT - Encyclopedia of Polymeric Nanomaterials. In: Kobayashi S, Müllen K (eds). Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 1167–1175 (2015).
- [11]. H. Uyama, H. Kikuchi, S. Kobayashi, One-Shot Synthesis of Polyester Macromonomer by Enzymatic Ring-Opening Polymerization of Lactone in the Presence of Vinyl Ester, *Chemistry Letters* 24 (1995) 1047–1048. Doi: 10.1246/cl.1995.1047
- [12]. D.S. Breslow, G.E. Hulse, A.S. Matlack, Synthesis of Poly- β -alanine from Acrylamide. A Novel Synthesis of β -Alanine1, *Journal American Chemistry Society* 79 (1957) 3760–3763. Doi: 10.1021/ja01571a039
- [13]. K. Yamaguchi, Y. Minoura, Hydrogen-transfer polymerization of acrylamide and methacrylamide with optically active basic catalysts, *Journal of Polymer Science Part A-1 Polymer Chemistry* 10 (1972) 1217–1231. Doi: 10.1002/pol.1972.150100425
- [14]. T. Iwamura, I. Tomita, M. Suzuki, T. Endo, Hydrogen-Transfer Polymerization of Vinyl Monomers Derived from 4-Methylbenzoyl Isocyanate and Acrylamide Derivatives, *Journal of Polymer Science Part A Polym Chem* 37 (1999) 465–472. Doi: 10.1002/(SICI)1099-0518(19990215)37:4<465::AID-POLA10>3.0.CO;2-3
- [15]. E. Çatiker, O. Güven, B. Salih, Novel hydrophobic macromonomers for potential amphiphilic block copolymers, *Polymer Bulletin* 75 (2018) 47–60. Doi: 10.1007/s00289-017-2014-2
- [16]. H. Nakayama, T. Higashimura, S. Okamura, Base-Catalyzed polymerization of vinyl acetamide and allyl cyanide, *Journal of Macromolecular Science Part A - Chemistry* 2 (1968) 53–68. Doi: 10.1080/00222336808053347
- [17]. H. Wexler, Migrational polymerization of methacrylamide, *Die Makromolekulare Chemie* 115 (1968) 262–267. Doi: 10.1002/macp.1968.021150123
- [18]. H. Kouzai, Hydrogen Transfer polymerization of acrylamide and its derivatives by sodium catalyst. *Kobunshi Ronbunshu* 61 (2004) 483–488. Doi: 10.1295/koron.61.483
- [19]. T. Otsu, B. Yamada, M. Itahashi, T. Mori, Hydrogen-transfer polymerization of methyl-substituted acrylamides, *Journal of Polymer Science Polymer Chemistry Edition* 14 (1976) 1347–1361. Doi: 10.1002/pol.1976.170140605
- [20]. I. Yoshikyuki, K. Kazuko, K. Yukio, Y. Shimizu, H. Arita, Y. Kozai, Hydrogen transfer polymerization of acrylamide derivatives by sodium naphthalene, *Kobunshi Ronbunshu* 44 (1987) 451–460. Doi: 10.1295/koron.44.451
- [21]. S. Okamura, Y. Oishi, T. Higashimura, T. Senoo, The study on the transition polymerization of methacrylamide, *Kobunshi Kagaku* 19 (1962) 323–327. Doi: 10.1295/koron1944.19.323
- [22]. R. Liu, K.Z. Vang, P.K. Kreeger, S.H. Gellman, K.S. Masters, Experimental and computational analysis of cellular interactions with nylon-3-

- bearing substrates, *Journal Biomedical Material Research - Part A* 100A (2012) 2750–2759. Doi: 10.1002/jbm.a.34211
- [23]. E. Çatiker, E. Konuk, T. Gültan, M. Gümüşderelioğlu, Enhancement of scaffolding properties for poly(3-hydroxybutyrate): blending with poly- β -alanine and wet electrospinning, *International Journal of Polymeric Materials and Polymeric Biomaterials* 68 (2019) 338–349. Doi: 10.1080/00914037.2018.1552862
- [24]. L. R. Liu, K.S. Masters, S.H. Gellman, Polymer chain length effects on fibroblast attachment on nylon-3-modified surfaces, *Biomacromolecules* 13 (2012) 1100–1105. Doi: 10.1021/bm201847n
- [25]. M.R. Lee, S.S. Stahl, S.H. Gellman, K.S. Masters, Nylon-3 copolymers that generate cell-adhesive surfaces identified by library screening, *Journal American Chemistry Society* 131 (2009) 16779–16789. Doi: 10.1021/ja9050636
- [26]. B.S. Thorat Gadgil, N. Killi, G.V.N. Rathna, Polyhydroxyalkanoates as biomaterials, *Medchemcomm* 8 (2017) 1774–1787. Doi: 10.1039/c7md00252a
- [27]. G.Q. Chen, J. Zhang, Microbial polyhydroxyalkanoates as medical implant biomaterials, *Artificial Cells, Nanomedicine, and Biotechnology* 46 (2018) 1–18. Doi: 10.1080/21691401.2017.1371185
- [28]. Ł. Kaniuk, U. Stachewicz, Development and Advantages of Biodegradable PHA Polymers Based on Electrospun PHBV Fibers for Tissue Engineering and Other Biomedical Applications, *ACS Biomaterial Science Engineering* 7 (2021) 5339–5362. Doi: 10.1021/acsbiomaterials.1c00757
- [29]. S. Penczek, M. Cypryk, A. Duda, P. Kubisa, S. Słomkowski, Living ring-opening polymerizations of heterocyclic monomers, *Progress in Polymer Science* 32 (2007) 247–282. Doi: 10.1016/j.progpolymsci.2007.01.002
- [30]. O. Nuyken, S.D. Pask, Ring-Opening Polymerization—An Introductory Review, *Polymers (Basel)* 5 (2013) 361–403. Doi: 10.3390/polym5020361
- [31]. K. Roos, Polyethers and polyamide-3 synthesis by monomer activated anionic polymerization, Doctoral Thesis, University of Bordeaux (2016).
- [32]. W.F. Su, Ring-Opening Polymerization BT - Principles of Polymer Design and Synthesis. In: Su W-F (ed). Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 267–299 (2013).
- [33]. A. Duda, A. Kowalski, Thermodynamics and Kinetics of Ring-Opening Polymerization. Handbook of Ring-Opening Polymer, Edited by P. Dubois, O. Coulembier, and J.-M. Raquez, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim pp. 1–51 (2009).
- [34]. I. Nifant'ev, P. Ivchenko, DFT Modeling of Organocatalytic Ring-Opening Polymerization of Cyclic Esters: A Crucial Role of Proton Exchange and Hydrogen Bonding, *Polymers (Basel)* 11 (2019) 2078. Doi: 10.3390/polym11122078
- [35]. W. Zhao, Q. Wang, Y. Cui, J. He, Y. Zhang, Living/controlled ring-opening (co)polymerization of lactones by Al-based catalysts with different sidearms, *Dalton Transaction* 48 (2019) 7167–7178. Doi: 10.1039/C8DT03941K
- [36]. B. Savaş, E. Çatiker, T. Öztürk, E. Meyvacı, Synthesis and characterization of poly(α -methyl β -alanine)-poly(ϵ -caprolactone) tri arm star polymer by hydrogen transfer polymerization, ring-opening polymerization and “click” chemistry, *Journal Polymer Research* 28 (2021) 1–10. Doi: 10.1007/s10965-020-02367-z
- [37]. E. Çatiker, E. Sancaktar, Blends of poly(3-hydroxybutyrate) with poly(β -alanine) and its derivatives, *Journal of Applied Polymer Science* 131 (13) (2014). Doi: 10.1002/app.40484
- [38]. E. Çatiker, T. Filik, Direct Synthesis of Hyperbranched Poly(acrylic acid-co-3-hydroxypropionate), *International Journal of Polymer Science* 2015 (2015) 231059. Doi: 10.1155/2015/231059
- [39]. H. Abe, Thermal degradation of environmentally degradable poly(hydroxyalkanoic acid)s, *Macromolecular Bioscience* 6 (2006) 469–486. Doi: 10.1002/mabi.200600070
- [40]. A. Czerniecka-Kubicka, W. Frącz, M. Jasiorski, W. Błażejowski, B. Pilch-Pitera, M. Pyda, I. Zarzyka, Thermal properties of poly(3-hydroxybutyrate) modified by nanoclay, *Journal of Thermal Analysis and Calorimetry* 128 (2017) 1513–1526. Doi: 10.1007/s10973-016-6039-9
- [41]. E. Çatiker, T. Öztürk, M. Atakay, B. Salih, Synthesis and characterization of the ABA-type poly(ester-ether-ester) block copolymers, *Journal of Macromolecular Science Part A Pure Applied Chemistry* 57 (2020) 600–609. Doi: 10.1080/10601325.2020.1745080
- [42]. J. Hong, D. Cho, T. Chang, W. Shim, D.S. Lee, (2003) Characterization of poly(ethylene oxide)-b-poly(l-lactide) block copolymer by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, *Macromolecular Research* 11 341–346. Doi: 10.1007/BF03218374
- [43]. M. Girod, M. Mazarin, T.N.T. Phan, D. Gigmes, L. Charles, Determination of block size in poly(ethylene oxide)-b-polystyrene block copolymers by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, *Journal of Polymer Science Part A Polymer Chemistry* 47 (2009) 3380–3390. Doi: 10.1002/pola.23414
- [44]. M. Chausson, A.S. Fluchère, E. Landreau, Y. Aguni, Y. Chevalier, T. Hamaide, N. Abdul-Malak, I. Bonnet, Block copolymers of the type poly(caprolactone)-b-poly(ethylene oxide) for the preparation and stabilization of nanoemulsions, *International Journal of Pharmacy* 362 (2008) 153–162. Doi: 10.1016/j.ijpharm.2008.06.007

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