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POLYMERIZATION OF VINYL ACETATE IN THE PRESENCE OF POLYLACTIDE-POLY(ETHYLENE GLYCOL) BLOCK-COPOLYMERS

Research article

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Abstract

This paper presents data on the polymerization of vinyl acetate in emulsions stabilized with biodegradable water-insoluble linear poly(lactide-poly(ethylene glycol)) block-copolymers. Since PEG is a readily soluble, highly polar polymer capable of forming a random coil, which can effectively sterically protect the surface of various nanoparticles and microparticles, block copolymers with various hydrophobic blocks can be obtained using PEG of different functionality and molecular weights. Diblock-copolymers were prepared from poly(ethylene glycol) methyl ether (MPEG, $M_n = 2\ 000$ Da) and *L*-lactide. The colloid-chemical properties of the copolymers have been studied. The block-copolymer was then used as the surfactant for the emulsion polymerization of vinyl acetate in the presence of potassium persulfate as an initiator. The effects of a new polymeric emulsifier on the physicochemical properties of obtained latexes were investigated.

Keywords: biodegradable polymers, surfactants, radical polymerization, polyvinyl acetate, polylactide.

ПОЛИМЕРИЗАЦИЯ ВИНИЛАЦЕТАТА В ПРИСУТСТВИИ БЛОК-СОПОЛИМЕРОВ ПОЛИЛАКТИД-ПОЛИЭТИЛЕНГЛИКОЛЬ

Научная статья

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Аннотация

В работе представлены данные по полимеризации винилацетата в эмульсиях, стабилизированных биоразлагаемыми водонерастворимыми линейными блок-сополимерами полилактид-полиэтиленгликоль. Поскольку ПЭГ является хорошо растворимым высокополярным полимером, способным эффективно стерически защищать поверхность различных наночастиц и микрочастиц, с использованием ПЭГ различной функциональности и молекулярной массы можно получать блок-сополимеры с различными гидрофобными блоками. Диблок-сополимеры были синтезированы на основе метилового эфира полиэтиленгликоля (МПЭГ, $M_n = 2000$ Да) и *L*-лактида. Изучены коллоидно-химические свойства данных сополимеров. Блок-сополимеры затем использовали в качестве ПАВ для эмульсионной полимеризации винилацетата в присутствии персульфата калия в качестве инициатора. Исследовано влияние нового полимерного ПАВ на физико-химические свойства полученных дисперсий.

Ключевые слова: биоразлагаемые полимеры, поверхностно-активные вещества, радикальная полимеризация, поливинилацетат, полилактид.

Introduction

Polyvinyl acetate (PVA, PVAc, poly(ethenyl ethanoate)) has a number of valuable specific properties and is widely used in various fields – from household products to materials for medical and biological purposes. The most important qualities of PVA are its universal adhesive and binding properties, high strength of fibers and film materials made with its use [1].

Research methods and principles

The main method for producing PVA is emulsion polymerization. Among emulsion monomers, vinyl acetate (VA) stands out for its good solubility in water in contrast to vinylbenzene, and this what determines the patterns of PVA synthesis [2], [3], [4]. The considerable reactivity of the VA radical results in heightened susceptibility to the existence of impurities, it is active in chain transfer reactions, and usually VA polymerization proceeds with an induction period [5], [6].

In radical polymerization of vinyl acetate, anionic and nonionic surfactants are most often used [7], [8]. A number of studies have demonstrated the existence of nonionic high-molecular surfactants, for instance, pluronics (triblock-copolymers of a polyoxypropylene and two hydrophilic chains of polyoxyethylene). This can lead to promising stability for PVA particles [9], [10], [11]. According to multiple studies, the importance of environmental protection was highlighted by examining various factors, high-molecular surfactants that can decompose under natural conditions to innocuous low-molecular products are promising. These are amphiphilic block-copolymers based on lactic acid [12], [13], [14], [15].

Thus, in this work, we synthesized several biodegradable linear amphiphilic block-copolymers of L-lactide and ethylene glycol. The colloid-chemical properties of those synthesized compounds were evaluated, and the heterophase polymerization of vinyl acetate in their presence were studied.

Main results

3.1. Synthesis of the linear diblock-copolymers

Linear diblock-copolymers of L-lactide and poly(ethylene glycol) was produced by ring-opening polymerization of L-lactide using monofunctional poly(ethylene glycol) methyl ether with molecular weight of 2 000 g mol⁻¹ and stannous octoate (Sn(Oct)₂) as the initiating system. The synthesis was performed at 150 °C for 24 h, and the obtained copolymers were separated from the catalyst and monomer residues by double reprecipitation in the tetrahydrofuran/(hexane – ethanol) system, followed by drying to a constant weight in a vacuum oven. The synthesis scheme is illustrated in Figure 1.

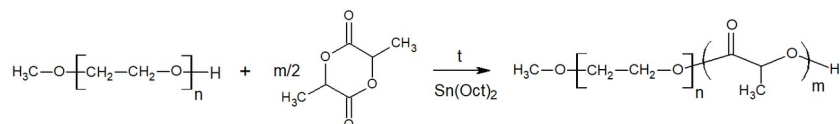


Figure 1 - Reactions pathways in the synthesis of PLLA-MPEG block-copolymers

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3.2. Identification of copolymers with NMR spectroscopy and its results

The identification of copolymers and their number-average molecular weight (\overline{Mn}) were accomplished by employing ¹H-NMR spectroscopy using «Bruker» NMR spectrometer (600 MHz). CDCl₃ was used as a solvent at room temperature and tetramethylsilane was used as an internal standard. The weight-averaged molecular weight (\overline{Mw}) and the PDI ($\overline{Mw}/\overline{Mn}$) were estimated by using gel permeation chromatography (GPC), which was conducted on a «Knauer» analyzer system (PL-GEL 5u MIXC 300×7.5 mm columns). The eluent was tetrahydrofuran (THF) flowing at a rate of 1.0 mL/min at 40 °C. The chemical structure of copolymers was determined according to the literature data [13], [17], [18], [19]. The copolymers' characteristics are presented in Table 1.

Table 1 - Characteristics of polylactide-poly(ethylene glycol) block-copolymers

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sample	\overline{Mn} (block-copolymers) ^a	\overline{Mn} (PLA chain) ^a	$(\overline{Mw}/\overline{Mn})^b$
PLLA ₁₀ -MPEG ₄₅	2 700	720	1.2
PLLA ₄₀ -MPEG ₄₅	4 860	2 880	1.5
PLLA ₆₀ -MPEG ₄₅	6 300	4 200	1.7

Note: ^aDetermined by ¹H-NMR. ^bDetermined by GPC (eluent: THF at 40 °C)

3.3. Investigation of colloidal chemical characteristics

The colloidal chemical characteristics of PLLA-MPEG block-copolymers were investigated. The interfacial tension and surface tension of the solutions were determined at room temperature by using a KRÚSS K9 surface tension tensiometer. It has been discovered that all copolymers decrease the interfacial tension to levels below 20 mN/m, aligning with the information found in the literature regarding copolymers containing polylactide [20], [21], [22].

3.4. The use of synthesized copolymers in the polymerization of vinyl acetate as surfactants

Linear and hyperbranched poly(ethylene oxide)-containing copolymers with high biocompatibility, obtained on the basis of aliphatic copolyesters, whose hydrophilic blocks are formed by polyethers, and hydrophobic blocks are formed by polymers of hydroxyacids (glycolic, lactic, hydroxybutyric, etc.), can be ranged among such biodegradable surfactants. It is known that the hydrolysis of such amphiphilic macromolecules leads to decomposition into environmentally harmless natural hydroxyacids and biocompatible oligomers [23], [24], [25], [26].

The use of water-insoluble surfactants in the heterophase polymerization of vinyl monomers is seen as a promising approach to producing polymer suspensions with a narrow particle size distribution (PSD). Biodegradable polyesters have been demonstrated to be exceptional stabilizers of polymer microspheres and hold a distinctive position among water-insoluble surfactants [12], [14].

The PLLA₆₀-MPEG₄₅ block copolymers were employed as a surfactant in the emulsion polymerization of vinyl acetate with potassium persulfate (PPS) as the initiator. Vinyl acetate (Fluka) with a basic substance content of ≥99 % was used as a monomer, and PPS (Sigma-Aldrich) with a basic substance content of 99.9% was used as an initiator. The vinyl acetate polymerization took place at a temperature 60±0.5 °C using a monomer-to-water volume ratio of 1:9. The initiator concentration was 1 wt % based on VA, while the surfactant concentration was 1.0 wt % per monomer.

3.5. Evaluation of the polymerization process using dilatometry method

Dilatometry is based on the fact that the density of a polymer is slightly higher than the density of its constituent monomer, causing the polymerization medium to contract over time. By employing a polymerization vessel equipped with a narrow capillary at the upper part, this shrinkage can be precisely tracked by assessing the variation in meniscus elevation over time [12], [27]. Polymerizations were monitored to about 99.9% conversion. The kinetic curves in the coordinates' conversion – time of VA polymerizations are clearly seen in figure 2. The complete conversion of VA is achieved within from 150 to 250 min.

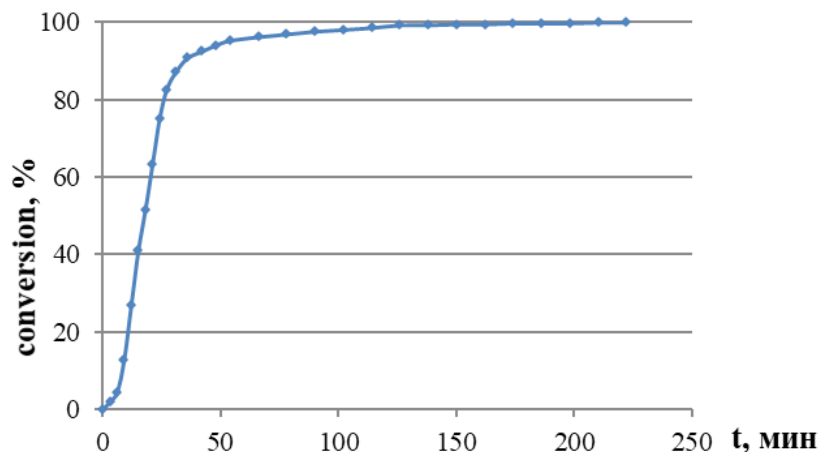


Figure 2 - Conversion – time curves obtained for vinyl acetate (VA) polymerization at 60 °C in the presence of PLLA₆₀-MPEG₄₅

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Note: volume ratio of VA : water = 1 : 9, [surfactant] = 1.0 wt %, [PPS] = 1.0 wt %

3.6. Investigation of the sizes and ξ -potential of the obtained PVA particles

The sizes of the obtained nanoparticles were estimated by the DLS method. The photomicrographs of PVA particles show that the PSD is narrow (figure 3). One notable aspect of this polymerization process is the creation of stable polymer suspensions that are distinguished by a narrow PSD. This allowed for the synthesis of a PVA suspension with particle sizes of approximately 0.7 μm .

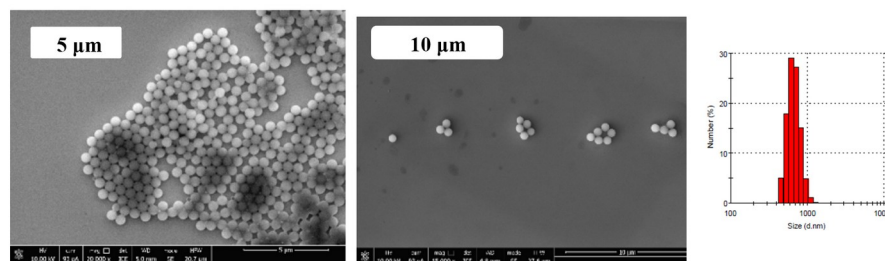


Figure 3 - Photomicrographs and histogram of particle size distribution of polyvinyl acetate suspension

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The ξ -potential values of the resulting polymer suspension were measured at -20 mV. This occurs even when the surfactant concentration is significantly lower than those required when using water-soluble ionic and nonionic surfactants at equivalent polymer content within the particle volume.

Conclusion

Thus, the synthesized biodegradable linear amphiphilic block-copolymers of L-lactide and ethylene glycol were comprehensively investigated. The high surface activity of polylactide-poly(ethylene glycol) block-copolymers and their capacity to generate thick interfacial adsorption layers on the polymer particle surfaces provide a rationale for the system's stability during polymerization.

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Конфликт интересов

Не указан.

Рецензия

Все статьи проходят рецензирование. Но рецензент или автор статьи предпочли не публиковать рецензию к этой статье в открытом доступе. Рецензия может быть предоставлена компетентным органам по запросу.

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Conflict of Interest

None declared.

Review

All articles are peer-reviewed. But the reviewer or the author of the article chose not to publish a review of this article in the public domain. The review can be provided to the competent authorities upon request.

Список литературы на английском языке / References in English

- Hassan C.M. Structure and Applications of Poly(vinyl alcohol) Hydrogels Produced by Conventional Crosslinking or by Freezing/Thawing Methods / C.M. Hassan, N.A. Peppas // *Advances in Polymer Science*. — 2000. — Vol. 153. — № 2. — P. 37-65.
- Zollars R.L. Kinetics of the emulsion polymerization of vinyl acetate / R.L. Zollars // *Journal of Applied Polymer Science*. — 1979. — Vol. 24. — № 5. — P. 1353-1370.
- Trivedi M.K. Emulsion Polymerization of Vinyl Acetate / M.K. Trivedi, K.R. Rajagopal, S.N. Joshi // *Journal of Polymer Science. Part A-1. Polymer Chemistry*. — 1983. — Vol. 21. — № 7. — P. 2011-2016.
- Pisarenko E.I. Emulsion polymerization of vinyl acetate initiated by organocobalt chelate complexes with a tridentate schiff base / E.I. Pisarenko, M.S. Tsar'kova, I.A. Gritskova [et al.] // *Polymer Science, Series A*. — 2004. — Vol. 46. — № 1. — P. 16-20.
- Moad G. *The Chemistry of Radical Polymerization* / G. Moad, D.H. Solomon. — Amsterdam: Elsevier, 2005. — 639 p.
- Gavat I. Grafting process in vinyl acetate polymerization in the presence of nonionic emulsifiers / I. Gavat, V. Dimonie, D. Donescu [et al.] // *Journal of Polymer Science: Polymer Symposia*. — 1978. — Vol. 64. — P. 125-240.
- Urquiola M.B. Emulsion polymerization of vinyl acetate using a polymerizable surfactant. II. Polymerization mechanism / M.B. Urquiola, V.L. Dimonie, E.D. Sudol [et al.] // *Journal of Polymer Science Part A: Polymer Chemistry*. — 1992. — Vol. 30. — № 1. — P. 2631-2644.
- Sosa N. A comparison of the characteristics of poly (vinyl acetate) latex with high solid content made by emulsion and semi-continuous microemulsion polymerization / N. Sosa, R.D. Peralta, R.G. Lopez [et al.] // *Polymer*. — 2001. — Vol. 42. — № 16. — P. 6923-6928.
- Binauld S. Emulsion Polymerization of Vinyl Acetate in the Presence of Different Hydrophilic Polymers Obtained by RAFT/MADIX / S. Binauld, L. Delafresnaye, B. Charleux [et al.] // *Macromolecules*. — 2014. — Vol. 47. — № 10. — P. 3461-3472.
- Magallanes Gonzalez G.S. Characterization of Poly(vinyl alcohol) during the Emulsion Polymerization of Vinyl Acetate using Poly(vinyl alcohol) as Emulsifier / G.S. Magallanes Gonzalez, V.L. Dimonie, E.D. Sudol [et al.] // *Journal of Polymer Science Part A: Polymer Chemistry*. — 1996. — Vol. 34. — № 5. — P. 849-862.
- Carra S. Grafting and adsorption of poly(vinyl) alcohol in vinyl acetate emulsion polymerization / S. Carra, A. Slipevich, A. Canevarolo [et al.] // *Polymer*. — 2005. — Vol. 46. — № 4. — P. 1379-1384.
- Gomzyak V.I. Heterophase Polymerization of Styrene in the Presence of Boltorn Polyester Polyol / V.I. Gomzyak, N.E. Artamonova, I.D. Kovtun [et al.] // *Polymer Science, Series B*. — 2020. — Vol. 62. — № 1. — P. 22-29.
- Gomzyak V.I. Biodegradable polymer materials for medical applications: from implants to organs / V.I. Gomzyak, V.A. Demina, E.V. Razuvaeva [et al.] // *Fine Chemical Technologies*. — 2017. — Vol. 12. — № 5. — P. 5-20.
- Istratov V.V. Amphiphilic Linear-Branched Copoly lactides and Disperse Systems on Their Basis / V.V. Istratov, V.I. Gomzyak, T.V. Krupina [et al.] // *Polymer Science, Series B*. — 2017. — Vol. 59. — № 6. — P. 730-736.
- Gomzyak V. I. Physico-chemical properties of biodegradable hyperbranched polyester polyol based on 2,2-bis(methylol)propionic acid / V.I. Gomzyak, A.A. Puchkov, N.E. Artamonova [et al.] // *Fine Chemical Technologies*. — 2018. — Vol. 13. — № 4. — P. 67-73.
- Murphy K.A. Synthesis, self-assembly and adsorption of PEO-PLA block copolymers onto colloidal polystyrene / K.A. Murphy, J.M. Eisenhauer, D.A. Savin // *Journal of Polymer Science, Part B: Polymer Physics*. — 2008. — Vol. 46. — № 3. — P. 244-252.
- Nakajima M. Nano-Ordered Surface Morphologies by Stereocomplexation of the Enantiomeric Polylactide Chains: Specific Interactions of Surface-Immobilized Poly(D-lactide) and Poly(ethylene glycol)-Poly(L-lactide) Block Copolymers / M. Nakajima, H. Nakajima, T. Fujiwara [et al.] // *Langmuir*. — 2014. — Vol. 30. — № 46. — P. 14030-14038
- Domanska I.M. A Comprehensive Investigation of the Structural, Thermal, and Biological Properties of Fully Randomized Biomedical Polyesters Synthesized with a Nontoxic Bismuth(III) Catalyst / I.M. Domanska, A. Zgadzaj, S. Kowalczyk [et al.] // *Molecules*. — 2022. — Vol. 27. — № 3. — P. 1139-1155.
- Mai S.M. Synthesis and characterization of block copolymers of polyoxyethylene and polylactide with different architectures / S.M. Mai, A. Abbot, D. Norton [et al.] // *Macromolecular Chemistry and Physics*. — 2009. — Vol. 210. — № 10. — P. 840-851.
- Gul'tekinoglu M. Honeycomb-like PLGA-b-PEG Structure Creation with T-junction Micro Droplets / M. Gul'tekinoglu, X. Jiang, C. Bayram [et al.] // *Langmuir*. — 2018. — Vol. 34. — № 27. — P. 7989-7997.

21. Hadjizadeh A. A Facile Approach for the Mass Production of Submicro/Micro Poly (Lactic Acid) Fibrous Mats and Their Cytotoxicity Test towards Neural Stem Cells / A. Hadjizadeh, H. Savoji, A. Ajji // *BioMed Research International*. — 2016. — P. 1-12.
22. Merkulova M.A. Easy size control of polymer nanoparticles obtained by emulsification—evaporation technique in a microfluidic reactor / M.A. Merkulova, N.S. Osipova, O.O. Maksimenko [et al.] // *Mendeleev Communications*. — 2021. — Vol. 31. — № 6. — P. 899-901.
23. Istratov V. Lineardendritic nonionic poly(propylene oxide)-polyglycerol surfactants / V. Istratov, H. Kautz, Y.K. Kim [et al.] // *Tetrahedron*. — 2003. — Vol. 59. — № 22. — P. 4017-4024.
24. Schneider K. Efficiency Boosting of Surfactants with Poly(ethylene oxide)-Poly(alkyl glycidyl ether)s: A New Class of Amphiphilic Polymers / K. Schneider, P. Verkoyen, M. Krappel [et al.] // *Langmuir*. — 2020. — Vol. 36. — № 33. — P. 9849-9866.
25. Kunze L. Nonionic Aliphatic Polycarbonate Diblock Copolymers Based on CO₂, 1,2-Butylene Oxide, and mPEG: Synthesis, Micellization, and Solubilization / L. Kunze, T. Shih-Yu, R. Schweins [et al.] // *Langmuir*. — 2019. — Vol. 35. — № 15. — P. 5221-5231.
26. Andrade B. Nonionic Surfactant Properties of Amphiphilic Hyperbranched Polyglycerols / B. Andrade, S.N. Knewstubb, K. Harris [et al.] // *Langmuir*. — 2020. — Vol. 36. — № 34. — P. 10103-10109.
27. Thickett S.C. Emulsion polymerization: State of the art in kinetics and mechanisms / S.C. Thickett, R.G. Gilbert // *Polymer*. — 2007. — Vol. 48. — № 24. — P. 6965-6991.