

Polymerization in Organized Systems

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1 Introduction

The effect of monomer organization on polymerization and polymer properties is illustrated by a critical survey of some typical polymerization experiments conducted in certain organized systems. For comparison, in most of the cases, the same polymerizations are performed under isotropic conditions. Monomer organization may prove, at least in principle, of critical importance in polymerization and it can be achieved in various ways including the use of thermotropic liquid crystalline media,¹⁻² orientation at liquid-liquid interfaces,³ and organization in micellar⁴⁻⁶ or vesicular media.⁷ It should be noted that these organized media are interrelated and recent findings established the fact that common molecular structural features lead to the formation of organized systems either in the bulk or in the dispersed phase. On the other hand, in discussing organized polymerization, we proceed from thermotropic liquid crystalline media to polymerization at liquid-liquid interfaces and then to micellar and vesicular phases to coincide with the historical development of the subject, and perhaps with the increasing complexity of the respective media.

The significance of polymerization in organized media is primarily attributable to its resemblance to biological reactions, which usually occur in organized systems.⁷ Furthermore, monomer organization may affect polymerization kinetics, polymer structure, and specifically microstructure, a polymer property that is directly related to the organization of the reacting monomers. Among the polymers of scientific and technological value prepared by polymerization in organized media, are liquid-crystal polymers⁸ and polymeric surfactants,⁷ which, depending on their molecular structure, may form intra- and/or inter-molecular micelles⁹ or polymerized vesicles.⁷ The latter aggregates retain the vesicular structure of their monomeric counterparts and since they exhibit sufficient stability

¹ E. M. Barral II and J. F. Johnson, *J. Macromol. Sci., Rev. Macromol. Chem.*, 1979, **17**, 137.

² H. Keller and R. Hatz, *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim, 1980.

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⁵ J. M. Brown in *Colloid Science*, A Specialist Periodical Report, Vol. 3, The Chemical Society, London, 1977, p. 253.

⁶ E. J. R. Sudhåter, G. R. van de Langkruis, and J. B. F. N. Engberts, *Recueil*, 1980, **99**, 73.

⁷ J. H. Fendler *Membrane Mimetic Chemistry*, John Wiley and Sons, New York, 1982.

⁸ *Liquid Crystal Polymers in 'Advances in Polymer Science'*, Vol. 59, 60, 61 ed. M. Gordon, Springer-Verlag, Berlin - New York, 1984.

⁹ C. M. Paleos, C. I. Stassinopoulou, and A. Malliaris, *J. Phys. Chem.*, 1983, **87**, 251.

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Table of Contents Polymerization Of Organized Systems

1. Understanding the eBook Polymerization Of Organized Systems
 - The Rise of Digital Reading Polymerization Of Organized Systems
 - Advantages of eBooks Over Traditional Books
2. Identifying Polymerization Of Organized Systems
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Polymerization Of Organized Systems
 - User-Friendly Interface
4. Exploring eBook Recommendations from Polymerization Of Organized Systems
 - Personalized Recommendations
 - Polymerization Of Organized Systems User Reviews and Ratings
 - Polymerization Of Organized Systems and Bestseller Lists
5. Accessing Polymerization Of Organized Systems Free and Paid eBooks
 - Polymerization Of Organized Systems Public Domain eBooks
 - Polymerization Of Organized Systems eBook Subscription Services
 - Polymerization Of Organized Systems Budget-Friendly Options

6. Navigating Polymerization Of Organized Systems eBook Formats
 - ePub, PDF, MOBI, and More
 - Polymerization Of Organized Systems Compatibility with Devices
 - Polymerization Of Organized Systems Enhanced eBook Features
7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Polymerization Of Organized Systems
 - Highlighting and Note-Taking Polymerization Of Organized Systems
 - Interactive Elements Polymerization Of Organized Systems
8. Staying Engaged with Polymerization Of Organized Systems
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Polymerization Of Organized Systems
9. Balancing eBooks and Physical Books Polymerization Of Organized Systems
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Polymerization Of Organized Systems
10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
11. Cultivating a Reading Routine Polymerization Of Organized Systems
 - Setting Reading Goals Polymerization Of Organized Systems
 - Carving Out Dedicated Reading Time
12. Sourcing Reliable Information of Polymerization Of Organized Systems
 - Fact-Checking eBook Content of Polymerization Of Organized Systems
 - Distinguishing Credible Sources
13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
14. Embracing eBook Trends
 - Integration of Multimedia Elements

- Interactive and Gamified eBooks

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