

STUDY OF BLOCK COPOLYMER: A REVIEW

¹Arockia Dixon Jeyakumar, ²Indrali Sarpothar, ³Priscilla Agnel, ⁴A.G. Thokal

¹⁻³Undergraduate Students at Bharati Vidyapeeth College of Engineering,

³Assistant Professor at Bharati Vidyapeeth College of Engineering,

¹Department of Chemical Engineering,

¹Bharati Vidyapeeth College of Engineering, Navi Mumbai, India

Abstract: Research on block copolymers (BCPs) has played a critical role in the development of polymer chemistry, with numerous pivotal contributions that have advanced our ability to prepare, characterize, theoretically model, and technologically exploit this class of materials in a myriad of ways in the fields of chemistry, physics, material sciences, and biological and medical sciences. Experimental techniques have allowed the synthesis and characterization of a broad range of block copolymers with tailored compositions, architectures, and properties, resulting in astounding development. In this review, we briefly discussed the recent progress in BCP synthesis, followed by a discussion of the fundamentals of BCPs along with their applications.

Block copolymers are a fascinating class of polymeric materials belonging to a big family known as “soft materials.” This class of polymers is made by the covalent bonding of or more polymeric chains that are thermodynamically incompatible in most situations, resulting in a wide range of microstructures in bulk and solution.

Key Words: polymer chemistry, tailored compositions, properties, synthesis, covalent, nanostructures, potential applications.

I. INTRODUCTION

Block copolymers are generally defined as macro-molecules with linear and or radial arrangement of two or more different blocks of varying monomer composition. In the last decade, synthesis techniques have been greatly expanded, and block copolymers with well-defined compositions, molecular weights, and structures of very elaborate architectures can now be prepared using ionic and regulated free radical methods. Block copolymers are gaining popularity due to their unique solution and associative properties, which are a result of their molecular structure. With the introduction of live anionic polymerization, it is now feasible to make well-defined block copolymers with minimal poly dispersity.

New polymerization techniques, such as atom transfer radical polymerization, reversible addition-fragmentation chain transfer polymerization (RAFT), ring-opening polymerization, and click chemistry, have recently been developed, allowing for a greater variety of architectures and chemical compositions. When applied to membranes, block copolymers allow for precise nanoscale tuning and the combination of materials with different properties in a single membrane. Block copolymers are macromolecules made up of chemically dissimilar segments that are linked at the ends. Block copolymers are macromolecules made up of chemically dissimilar segments that are joined at the ends. A block copolymer is a polymer made up of molecules that are arranged in a linear pattern, with a block referring to a segment of the polymer. At least one constitutional or configurational characteristic of the monomeric units is absent from the adjacent portions of the molecule. The constitutional feature of a block copolymer is that each of the blocks is made up of units derived from a specific monomer species.

This description does not include branched structures whose branches are made up of blocks, *i.e.* star or radical block copolymers. Well-defined structures Block copolymers are capable of forming different ordered phases at nanoscopic length scales. When block copolymers are coupled with rigid templates of various shapes and sizes, limiting conditions severely limit the morphologies that the block copolymers may produce. The interaction of symmetry, length size, and polymer-wall interactions results in a variety of novel and complex morphologies not possible in bulk block copolymer systems, thus providing opportunities to engineer novel nanostructures. A significant number of experimental and theoretical research have yielded certain principles for the creation of limited block copolymer morphologies. There is a rapid development of research, every year, a large number of scientific publications on the synthesis, physical characteristics, and uses of block copolymers are published in top journals in the domains of polymer and material science.

II. Synthesis of Block Polymer

The best block copolymer synthesis is based on sequential anionic addition or ring opening polymerization techniques or on step-growth polymerization. These approaches enable the control of block integrity and sequential design, both of which are critical for attaining the best possible results. Although block copolymers are more difficult to prepare than random copolymers, they are not hampered by the co-monomer reactivity ratio restrictions of the latter. The different block copolymer segments can also be synthesised using a variety of processes. The applicability of step-growth techniques to block copolymers permits the synthesis of a wide spectrum of high performance compositions.

There are three principal methodologies for synthesis of block copolymers with well-defined structures:

2.1 Living Polymerization of different monomers by sequential additions

An AB diblock copolymer, poly(A)-block-poly(B), is created by adding a monomer (B) to a live polymer made from a monomer (A). Under the right circumstances, a broad range of block copolymers, such as ABA triblock copolymer, (AB)_n multiblock copolymer, and ABC triblock terpolymer, might be made by adding more of the matching monomers. Because the reactivity of the live polymer must always be sufficient for the quantitative initiation of the next monomer, the sequence in which monomers are added is critical for the success of block copolymerization.

2.2 The use of end- functional groups on an original polymer chain to initiate another living polymerization

This approach is beneficial when the second-stage polymerization mechanism is incompatible with the first-stage polymerization mechanism. The end-functionalized polymer, often called a macro initiator, is prepared by transforming active

species on a living polymer chain end into functional groups that can quantitatively initiate another living polymerization. Low initiation efficiency indicates that the final block copolymer contains unreacted parent polymer. Similarly, slow initiation always causes broadening of polydispersity.

2.3 End linking between different polymers through highly reactive functional groups

The advantage of this method is that the molecular weight and the segment ratio of block copolymer produced are predictable since molecular weights of the original end-functionalized polymers are known quantity. In addition, any combination of block segments may be allowed once the suitable end-functionalized polymer is obtained. On the other hand, the quantitative and stoichiometric reaction through end-functional groups is required to produce the pure block copolymer. Otherwise, the unreacted or the excess-used homopolymer contaminates the product.

III. Properties of Block polymer

- i. Block copolymers and graft copolymers share many basic properties. This is owing to the occurrence of intersegment chemical connections, which is a common characteristic among them. From a simplistic point of view, block and graft copolymers resemble incompatible physical blends in some respects and homogeneous random copolymers in others.
- ii. Such systems usually exhibit two-phase morphology, but this occurs on a micro-scale rather than the macroscale dimension of incompatible physical blends. This is related to the intersegment linkage's impact, which limits the separation of the phases to a certain amount.
- iii. The small domain size and excellent interphase adhesion resulting from this microphase morphology can produce a high degree of transparency and a good balance of mechanical properties. This behaviour reminds of homogeneous copolymers and is not typical of polymer blends. Many additional features, like as permeability and chemical resistance, are influenced by which section of the continuous phase is present.
- iv. The thermal properties of block copolymers resemble those of physical blends. They show a variety of thermal transitions, including glass transitions and/or crystalline melting points, which are unique to each component. Homogeneous random copolymers, on the other hand, have a single, composition-dependent glass transition temperature.
- v. Furthermore, while crystallinity is possible in block copolymers, due to long sequences, it is diminished or eliminated in the random systems due to a disruption of chain regularity. Due to the existence of long segments in block copolymers, these compounds may be used as emulsifiers or surfactants. The incompatibility of homopolymer blends, both in solution and in the solid state, is reduced by the addition of small quantities of the respective block copolymers.
- vi. In addition, blending a block copolymer with one of the respective homopolymers provides a means for achieving a fine dispersion of the "foreign" segment in the homopolymer matrix. Significant commercial products, such as impact-modified thermoplastics, make use of the above feature.
- vii. Block copolymers offer a clear advantage over graft copolymers. Since block copolymer synthetic techniques are more reliable and predictable, it is possible to achieve desired structures with greater precision. As a result, essential parameters including sequence design, segment duration and spacing, polydispersity, and contamination by homopolymer or undesired copolymer architectures are far better controlled.
- viii. These factors lead to a higher degree of morphological perfection in block copolymers, which, in turn, is reflected in superior physical properties. The idea of thermoplastic elastomeric behaviour is a novel invention stemming from block copolymer technologies.

IV. Applications of Block Copolymer

- i. Symmetrical star-shaped polymers have been found to be effective thermoplastic elastomers. Mechanical properties such as hardness, stretch regeneration, clarity, and thermostability benefit from their morphologies.
- ii. Copolyester TPEs are used in snowmobile tracks where stiffness and abrasion resistance are at a premium.
- iii. Light emitting conjugated polymers such as polythiophenes (PT), polyphenylene vinylenes (PPV), polyphenylene ethynylenes (PPE) and polyfluorenes (PF) are being screened for potential applications and PPVs find applications in various fields including optoelectronics, photovoltaics, nonlinear optics and bioimaging.
- iv. Upholstered sofa cushions, vehicle seat cushions and interior trim, carpet cushion, mattress padding, and solid-core mattress cores are all examples of flexible polyurethane foam applications
- v. Removal/Recovery of Organic/Inorganic Compounds from Contaminated Waters is done by using the micelle-forming ability of block copolymers. The removal/recovery of toxic organic compounds (as, i.e., halogenated and polyaromatic hydrocarbons) it is possible to do this from polluted water (coastal, soil, and ground). The organic compound is entrapped in the hydrophobic centre of the micelles, which are then removed and retrieved after being stabilised in water by the external hydrophilic shell.



Fig no. 4.1 Snowmobile tracks



Fig no. 4.2 olefins used as waterproof roofing

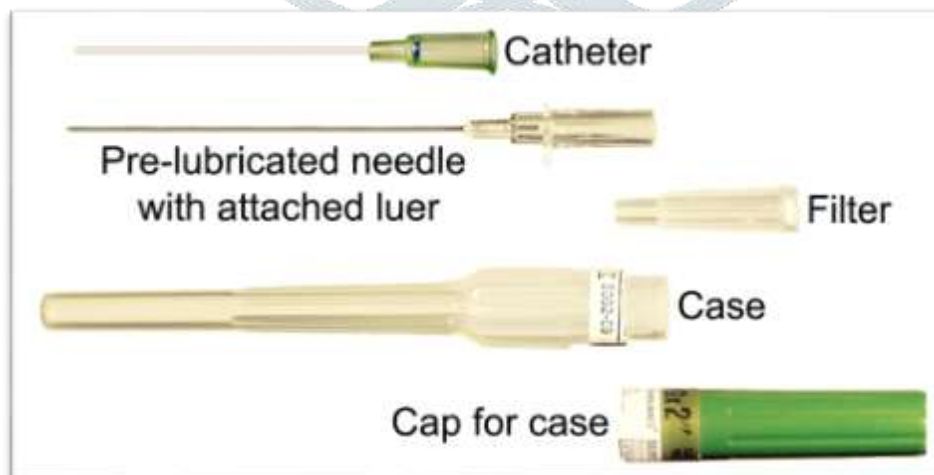


Fig no. 4.3 Catheters

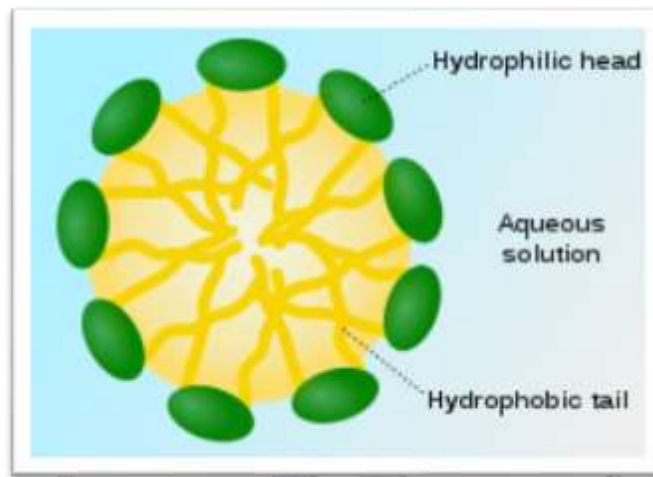


Fig no. 4.4 Micelle used as drug delivery

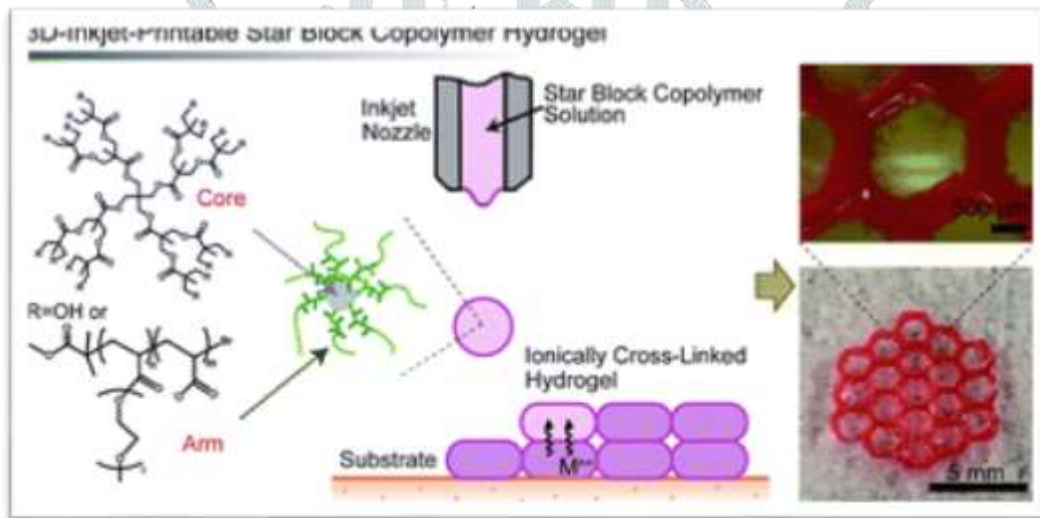


Fig no. 4.5 Hydrogel

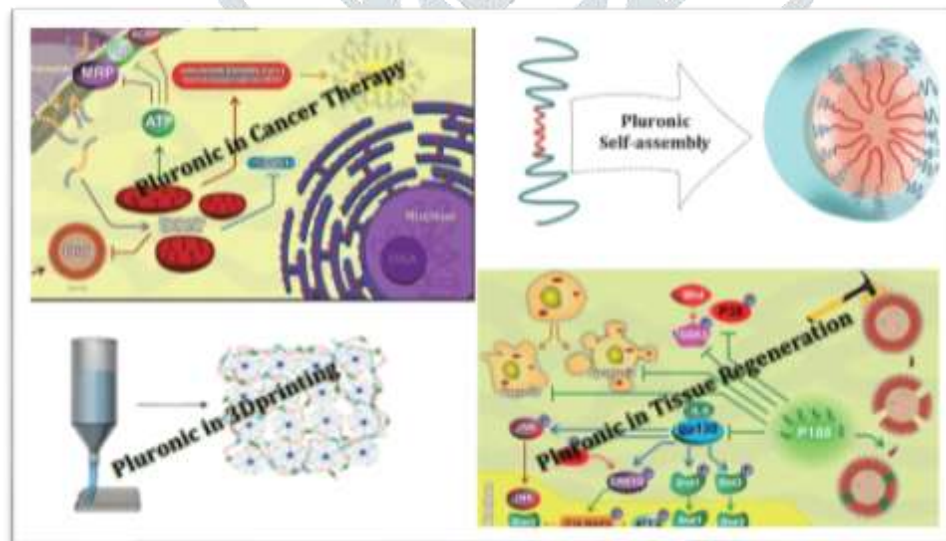


Fig no. 4.6 Poloxamers



Fig no. 4.7 Light diodes



Fig no. 4.8 Photovoltaics

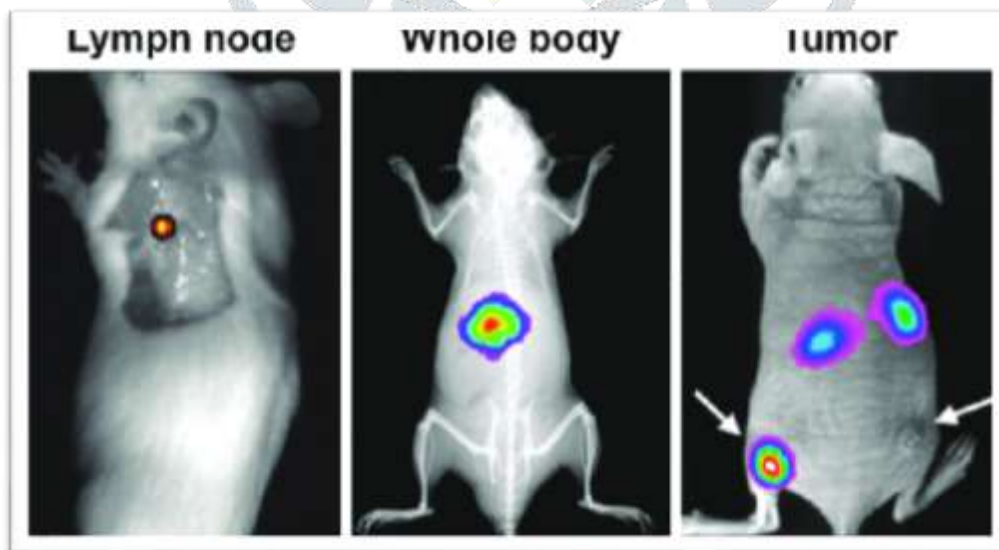


Fig no. 4.9 Bioimaging

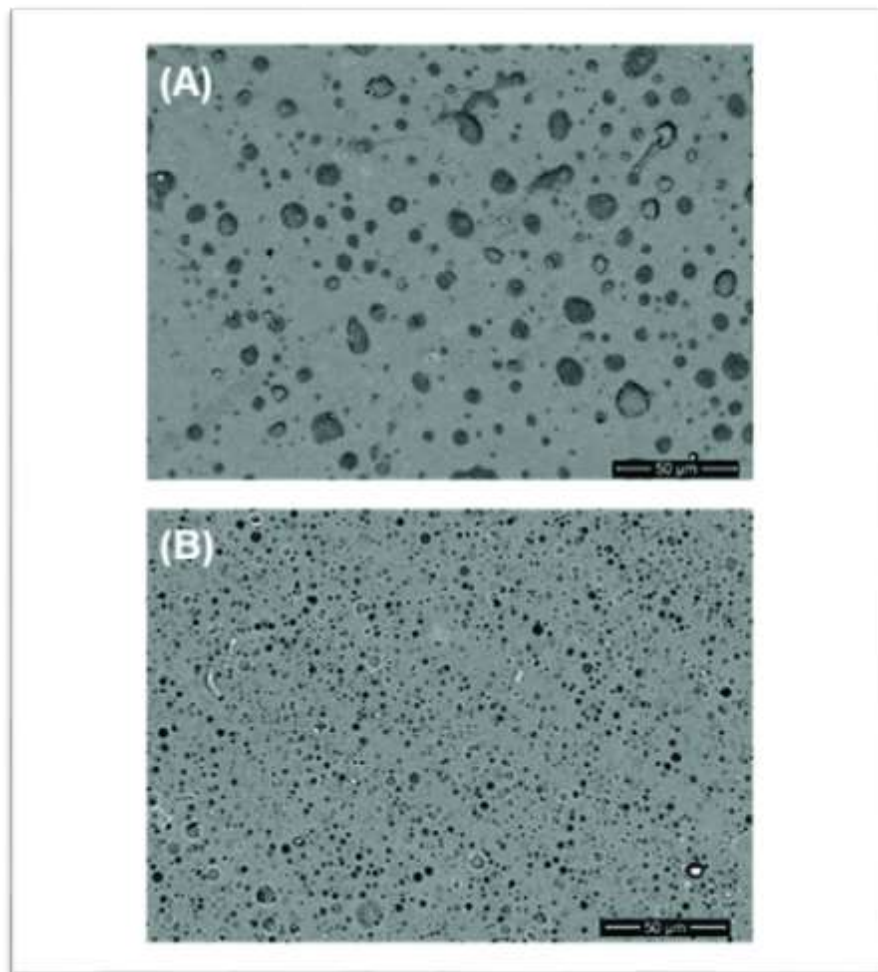


Fig no. 4.10 Stabilization of interfaces



Fig no 3.9 Automotive seats

V. Scope for Future

- i. The demands for increasing precision and functional complexity for BCPs at the molecular scale in conjunction with adaptability for self-assembled structures at nanoscale to meet the requirements of biomimetic materials and even life-supporting materials provide further impetus to advance the field of self-assembling BCPs.
- ii. The main concerns for humans in the future will be energy & resources, food, health, mobility & infrastructure and communication.
- iii. There is no doubt that polymers will play a key role in finding successful ways in handling these challenges. Polymers will be the new millennium's stuff, and the manufacture of polymeric components, i.e. green, sustainable, energy-efficient, high quality, low-priced, etc. will ensure that the best ideas are available all over the world.
- iv. Synthetic polymers have since a long time played a relatively important role in present-day medicinal practice. Synthetic polymers are used to make a variety of medical instruments, including artificial organs.
- v. It is possible that synthetic polymers may play an important role in future pharmacy, too. Polymer science can be used to reduce energy consumption and boost sustainable energy systems.
- vi. Biopolymers could especially increment as more solid adaptations are produced, and the cost to fabricate these bioplastics keeps on going fall.

- vii. Bio-plastics can supplant routine plastics in the field of their applications likewise and can be utilized as a part of various areas, for example, sustenance bundling, plastic plates, mugs, Cutlery, plastic stockpiling bags, and other items can help to save the ecosystem in this manner.
- viii. In areas of applications of plastics materials, a well-known long standing example is electrical industries have led to increasing acceptance of plastics for plugs, sockets, wire and cable insulations and for housing electrical and electronic equipment.
- ix. The major polymer targeting industries of the present day life includes Ceramic industries, in stem cell biology and Regenerative Medicine, packaging industries, in retorting method used for food processing automotive, aerospace, and electrical and computer sectors are also examples of industries.

VI. Conclusion

It is also illuminated an understanding of the concepts of self-assembly that promote the interaction of these block copolymers into polymer micelles, polymersomes, and polyelectrolyte complex micelles. Polymersomes with high stability, biocompatibility, and low fluidity stand out among them as promising candidates for in vivo molecular imaging and nanotherapeutics. The real-time challenge is to boost the explicit delivery of polymer micelles and polymersomes to the site of action, as well as their victorious diffusion capacity against infected cells, by designing and fabricating them. To achieve convenient drug distribution and imaging potency, clinical requirements must be considered and unified with improved drug half-life and enhanced cellular uptake. One of the current problems is the transport of medications across the body, followed by targeted delivery. As a result, pharmaceutical companies are also baffled by these tailored personalised nanomedicines. Another significant concern is the lack of compliance concerns that determine the safety of pharmaceutical drugs. Subsequently, the advent of living anionic polymerization and controlled radical polymerization techniques, and the development of efficient post-modification methodologies have enabled the synthesis of well-defined BCPs capable of self assembling in selective solvents. In this review, we present an overview on emerging trends of solution self-assembly of BCPs. Despite significant advances in these emerging fields on solution self-assembly of BCPs, multiple challenges remain to be tackled in future study.

VII. Reference

1. Allen R. D., Long T. E., McGrath J. E. (1986) *Polym. Bull.*
2. Almdal K., Mortensen K., Ryan A. J., Bates F. S. (1996) *Macromolecules*
3. Antkowiak T. A., Oberster A. E., Halasa A. F., Tate D. P. (1972) *J. Polym. Sci.*
4. Allcock H. R., Reeves S. D., Nelson J. M., Manners I. (2000) *Macromolecules*
5. Cao X., Sipos L., Faust R. (2000) *Polym. Bull.*
6. Faust R. (1999) *Polym. Prepr.*
7. Faust R. (2000) *Macromol. Symp.*
8. Faust R., Shaffer T. D. (Eds) (1997) *Cationic Polymerization: Fundamentals and Applications*,
9. ACS Symposium Series, Vol 665, Washington, DC.
10. Fodor Z., Faust R. (1994) *J. Macromol. Sci.*
11. Fodor Z., Faust R. (1995) *J. Macromol. Sci.*
12. Benoit D., Harth E., Fox P., Waymouth R. M., Hawker C. J. (2000) *Macromolecules*
13. Bignozzi M. C., Ober C. K., Laus M. (1999) *Macromol. Rapid Commun.*
14. Chiefan J., Chong Y. K., Ercole F., Krstina J., Jeffem J., Le T. P. T., Manadunne R. T.A.
15. Meijs G. F., Moad C. L., Moad G., Rizzardo E., Thang S. H. (1998) *Macromolecules*
16. Chong B. Y. K., Le T. P. T., Moad G., Rizzardo E., Thang S. H. (1999) *Macromolecules*
17. Davis K. A., Matyjaszewski K. (2001) *Macromolecules.*
18. Fukuda T., Terauchi T., Goto A., Tsujii Y., Miyamoto T. (1996) *Macromolecules.*
19. Gabaston L. I., Furlong S. A., Jackson R. A., Armes S. P. (1999) *Polymer.*
20. Georges M. K., Veregin R. P. N., Kazmaier P. M., Hamer G. K. (1993) *Macromolecules.*
21. Granel C., DuBois P., Jerome R., Teyssie P. (1996) *Macromolecules.*
22. Halari I., Pispas S., Hadjichristidis N. (2001) *J. Polym. Sci. Part A: Polym. Chem.*
23. Hawker C. J. (1994) *J. Am. Chem. Soc.*
24. Kato M., Kamigaito M., Sawamoto M., Higashimura T. (1995) *Macromolecules.*
25. Keoshherian B., Georges M. K., Boils-Boissier D. (1995) *Macromolecules.*
26. Keoshkerian B., Georges M., Quinlan M., Veregin R., Goodbrand B. (1998) *Macromolecule*