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FOCUS REVIEW

A viewpoint on block copolymer self-assembly revealed by time-resolved small-angle X-ray scattering

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Abstract

Time-resolved small-angle X-ray scattering (TR-SAXS) is an indispensable technique for directly monitoring in situ kinetic processes in soft matter, providing real-time structural information from nanometer to micrometer length scales. This Focus Review summarizes recent significant advances in understanding the self-assembly kinetics of block copolymers in solution, primarily revealed through TR-SAXS. The review is structured into three key sections, each addressing distinct driving forces and mechanisms. First, we discuss the formation and transformation of micelles, predominantly driven by non-covalent interactions like van der Waals forces and hydrophobic interactions, leading to the spontaneous association of amphiphilic block copolymers in selective solvents. Next, we cover polyelectrolyte complex micelles and vesicles, where self-assembly is initiated by electrostatic interactions, as mixing oppositely charged block polyelectrolytes in aqueous media forms complex coacervate structures. Finally, we present polymerization-induced self-assembly (PISA), a unique approach involving the in situ formation and evolution of block copolymer nanostructures as a monomer is polymerized from a pre-existing polymer chain, simultaneously achieving block copolymer synthesis and self-assembly. Through these examples, we highlight the power of TR-SAXS in elucidating the intricate kinetic pathways and underlying mechanisms governing block copolymer self-assembly.

Introduction

Block copolymers, composed of two or more chemically distinct polymer blocks covalently linked, exhibit a remarkable ability to self-assemble into diverse nanostructures when placed in selective solvents. This spontaneous organization, driven by thermodynamic forces, leads to a wide variety of morphologies including spherical micelles, cylindrical micelles, vesicles, and more complex hierarchical structures [1–3]. Understanding the kinetics and mechanisms governing these self-assembly processes is not just a matter of fundamental scientific curiosity; it is also critically important for the rational design and synthesis of functional nanomaterials with tailored properties, applicable in fields ranging from drug delivery and diagnostics to advanced coatings and energy storage [4–6].

For decades, researchers have made significant strides in characterizing the equilibrium structures of block copolymer assemblies [7, 8]. However, truly elucidating the dynamic pathways and transient intermediate states that occur during their formation and transformation remains a substantial challenge. This is where time-resolved small-angle X-ray scattering (TR-SAXS) has become a crucial technique owing to recent developments in synchrotron radiation X-ray sources and detectors. By providing in situ real-time structural information on nanometer to micrometer length scales with high temporal resolution, TR-SAXS allows for direct monitoring of kinetic processes in soft matter, offering unparalleled insights into the transient structures and mechanistic details that are otherwise difficult to access.

Several reviews have previously explored aspects of block copolymer self-assembly. For example, Lund et al. provided a broad overview of TR-SAXS and time-resolved small-angle neutron scattering (TR-SANS) studies focusing on block copolymer micelles [8]. More recently, Lodge et al. reviewed the dynamics and equilibration mechanisms

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with a specific focus on spherical micelles [9], and Narayanan summarized SAXS studies on the broader dynamics of colloids [10]. Building upon these foundational contributions, this Focus Review aims to provide an overview of the recent advances in understanding block copolymer self-assembly kinetics in dilute solutions, predominantly as revealed through the application of TR-SAXS, with a particular emphasis on the authors' viewpoint and its context within the broader field. This review will prioritize discussing what has been revealed thus far by TR-SAXS regarding these dynamic processes rather than delving into the intricate details of SAXS data analysis methodologies. We particularly highlight studies concerning (i) the formation and transformation of micelles driven by van der Waals and hydrophobic interactions; (ii) the self-assembly of polyelectrolyte complex micelles and vesicles formed through electrostatic interactions; and (iii) polymerization-induced self-assembly (PISA), a dynamic process where structural evolution occurs concurrently with polymer synthesis. Through these distinct categories, we aim to underscore the unique power of TR-SAXS in advancing our fundamental understanding of block copolymer self-assembly and its dynamic evolution.

Formation and transformation of micelles

The study of micelle formation dates back to the 1960s, with turbidity changes during the micellization of low-molecular-weight surfactants in aqueous solution revealing two distinct relaxation times, suggesting multi-step kinetic processes [11]. Nearly five decades later, the advent of high-flux synchrotron X-ray sources and rapid detection systems enabled Lund et al. to successfully monitor the initial stages of polymeric micelle formation by TR-SAXS [12]. They employed a stopped-flow apparatus (Fig. 1) to rapidly mix a poly(ethylene propylene)-*block*-poly(ethylene oxide) (PEP_{16}-*b*-PEO_{497}) solution in *N,N*-dimethylformamide (DMF) with an aqueous solution containing 20 mol% DMF. This rapid mixing (1:1 ratio) yielded a 10 mol% DMF aqueous mixture, thereby inducing micelle formation. The SAXS scattering function in pure DMF exhibited a nearly angle-independent profile. However, immediately after mixing ($t = 14.5$ ms), a sharp increase in the scattering intensity at a low angle was observed, and a distinct angle dependence emerged, signifying the onset of micelle formation. This intensity continued to increase over time, reflecting the growth and maturation of the micellar structures. Figure 2 shows the time dependence of the mean aggregation number of the spherical micelles, derived from their scattering functions. A key finding was that micelle growth accelerated with increasing copolymer concentration, exhibiting a characteristic two-step time dependence at all the concentrations studied. This suggests a complex kinetic pathway involving initial nucleation and subsequent growth phases through unimer exchange. It is highly probable that the unimer exchange process was dominant in the study by Lund et al. due to the specific characteristics of their copolymer: the relatively large degree of polymerization of the hydrophilic block (PEO_{497}) and the smaller degree of polymerization of the hydrophobic block (PEP_{16}). If the hydrophilic block had a significantly smaller degree of polymerization and the hydrophobic block a larger one, growth *via* fusion/fission processes could also occur. Kalkowski et al. further extended these investigations, demonstrating the ability of TR-SAXS to probe micellization kinetics with millisecond temporal resolution [13].

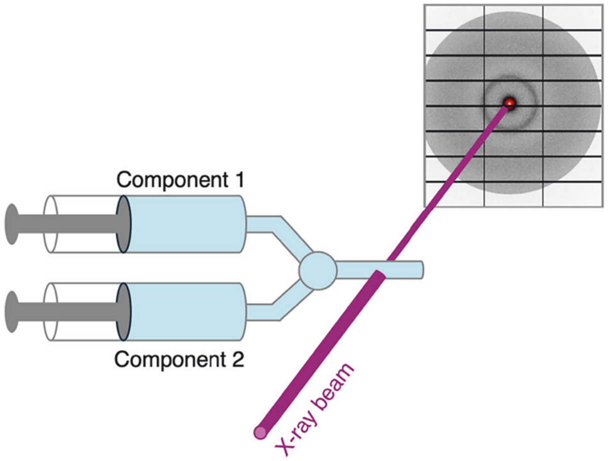

Fig. 1 Schematic illustration of SAXS coupled with a stopped-flow apparatus

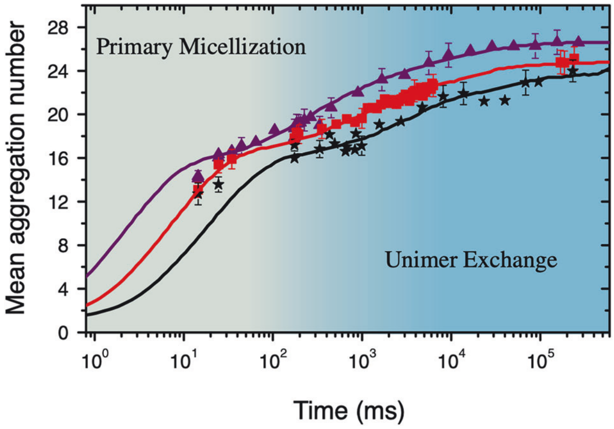

Fig. 2 Time dependence of the mean aggregation number, extracted from the fits for all three total volume fractions: 0.125% (stars); 0.25% (squares), and 0.5% (triangles). The solid lines represent fits using the kinetic model. Reproduced with permission from ref. [12]. Copyright 2009 American Physical Society

Beyond mere formation, TR-SAXS is also exceptionally useful for studying the morphological transformation of micelles. For example, Lund et al. investigated the morphological transition of poly(ethylene propylene)-*block*-

poly(ethylene oxide) (PEP_{17}-*b*-PEO_{34}) micelles from cylinders to spheres [14]. They dissolved the block copolymer in a mixture of 51 mol% deuterated DMF (d-DMF) in water and then triggered the transition by rapidly mixing this solution with additional d-DMF (1:1 ratio) using a stopped-flow apparatus. By employing TR-SAXS as well as TR-SANS, they were able to monitor the transition in situ, providing a more accurate and comprehensive view of the micellar changes. The scattering data were modeled assuming the coexistence of cylindrical and spherical micelles, which enabled quantitative determination of the fraction of each morphology and the diameter of the spherical micelles over time. A crucial observation was the constant length of the cylindrical micelles throughout the transition, leading the authors to conclude that an all-or-none transition occurred rather than a gradual shortening of the cylinders. Furthermore, they reported a slow but continuous increase in the diameter of the spherical micelles during the later stages of the transition, strongly suggesting an Ostwald ripening process where the average association number of the spherical micelles increases as larger micelles grow at the expense of smaller ones. These studies vividly demonstrate the unique capability of TR-SAXS to unveil the subtle, yet critical, kinetic details of block copolymer self-assembly and morphological transitions.

Polyelectrolyte complex micelles and vesicles

When a polycation and a polyanion are mixed in an aqueous solution, a polyelectrolyte complex (PEC) is formed, driven primarily by strong electrostatic interactions or by the entropy gain associated with the release of condensed counterions. This process can be viewed as a type of liquid–liquid phase separation, often referred to as coacervation. Early studies in the 1940s reported this phenomenon [15, 16], and several groups investigated its kinetic process using time-resolved light scattering, typically at a single scattering angle, which provided limited structural information. The present author and coworkers [17] employed time-resolved ultra-small-angle X-ray scattering (TR-USAXS) coupled with a stopped-flow apparatus [18] and revealed that the very initial association of oppositely charged polyelectrolytes is extremely rapid («2.5 ms) and is below the detection limit of mixing and scattering techniques. It is worth noting that while the study [17] was performed at the ID02 beamline, ESRF, in 2017, the dead time was reduced to 2.0 ms by 2021 [19].

Regarding polyelectrolyte complex micelles, the group of Lund has extensively studied the kinetic pathways for micelle formation from oppositely-charged polymers with electroneutral blocks by TR-SAXS [20–22]. In their work, electrostatic interactions drive the formation of these micelles, which contrasts with conventional micelles primarily formed by hydrophobic and/or van der Waals interactions. Their work has provided crucial insights into the formation of spherical polyelectrolyte complex micelles. Wu et al. also reported spatiotemporal formation and growth kinetics of polyelectrolyte complex micelles with millisecond resolution, further demonstrating the power of TR-SAXS in this field [23]. However, the very initial stages in polyelectrolyte complex formation, specifically the association between a single polyanion and a single polycation, have not been observed by TR-SAXS.

The authors have also studied the morphological transitions of polyelectrolyte complex micelles and vesicles, formed from cationic–neutral and anionic–neutral block copolymers. This system exhibits morphological changes—from spherical micelles to rod-like micelles and vesicles—depending on the salt concentration and the mixing ratio of cationic and anionic polymers [24, 25]. What is particularly noteworthy is that, unlike most types of vesicle formation, which typically require the use of organic solvents for dissolution or mechanical/thermal treatment, polyelectrolyte complex vesicles can be formed simply by mixing in aqueous solution. Therefore, this inherent ability of the system to form polymeric vesicles upon simple mixing enables their observation through stopped-flow TR-USAXS measurements. Regarding the transition from rod-like to spherical micelles, we revealed that this occurs through a mechanism where the rod-like micelles are considered as chains of spherical micelles, and their linkages are randomly cleaved [26]. This conclusion is different from that of Lund et al. [14] as above, although direct comparisons may be limited due to differences in sample types, driving forces, and intermolecular interactions. It is worth noting that Lund et al. did not derive the molar mass of the cylindrical micelles, likely due to the limited range of the magnitude of the scattering vector.

For the transition from spherical or rod-like micelles to vesicles, it was found that disk-like micelles form as an intermediate structure, which then curves to become vesicles [27] (Fig. 3). The fundamental mechanism of vesicle formation was similar to that reported for low-molecular-weight surfactants [28], which have also been investigated by TR-SAXS. However, since polymeric vesicles possess thicker membranes, the increased energy required for curvature suggests that this curving process into vesicles represents a significant energy barrier. It is worth noting that the mechanism of polymeric vesicle formation (not polyelectrolyte complex vesicle) studied by liquid-phase transmission electron microscopy (TEM) [29] differs from the disk-curving mechanism; a phase-separation-mediated mechanism has been proposed. This alternative mechanism, however, has not yet been observed *via* TR-SAXS.

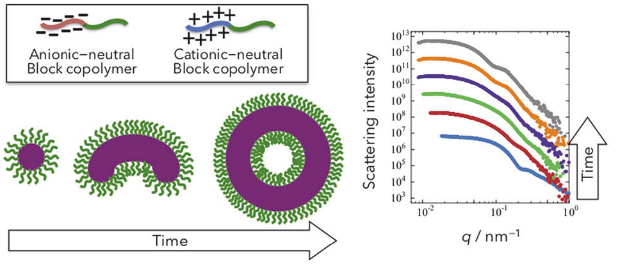

Fig. 3 Schematic illustration of the formation process and time-evolution of the USAXS profiles during polymer vesicle formation. Reproduced with permission from ref. [27]. Copyright 2022 American Chemical Society

Recent advances in the structural design of polyelectrolyte complex micelles were also reviewed by Marras et al. [30].

Polymerization-induced self-assembly (PISA)

The self-assembly processes discussed so far are typically induced by changes in the external environment of pre-formed polymers, such as alterations in added salt concentration, temperature, solvent composition, or mixing ratios of the polymers. In these scenarios, the degree of polymerization of the constituent blocks remains constant throughout the self-assembly and transformation process. In contrast, this section focuses on a distinct and increasingly important strategy in which polymerization itself induces the formation and transformation of micelles and vesicles. This phenomenon, widely known as PISA, involves the in situ growth of a solvophobic block from the end of a solvophilic polymer chain in solution. As the newly formed block grows and reaches a critical chain length, the resulting amphiphilic block copolymer self-assembles (Fig. 4), with the micellar morphology often evolving as the polymerization proceeds.

The PISA process is fundamentally different from conventional self-assembly because the degree of polymerization continuously increases during the entire process of micelle formation, growth, and subsequent transformation. Hence, PISA typically occurs on a much slower timescale, ranging from minutes to hours. This slow kinetics can be readily monitored by TR-SAXS without stopped-flow device, even with laboratory-based SAXS instruments, unlike the rapid, millisecond-scale early stages of other self-assembly processes that necessitate high-flux synchrotron sources. However, since many polymerization reactions are inhibited by oxygen, samples must be deoxygenated and the cells sealed before measurement, often requiring techniques like working in a glove box.

The group of Armes has pioneered many aspects of PISA, being among the first to observe the growth of the spherical micelles (Fig. 5a) as well as sequential morphological evolution from spherical micelles to cylindrical micelles and then to vesicles as the polymerization progresses (Fig. 5b) [31, 32]. They extensively employed reversible addition–fragmentation chain transfer (RAFT) dispersion polymerization to synthesize diblock copolymers for their studies. During the PISA process, the packing parameter ($p = v/(a_0L)$), which describes the geometric constraints on block copolymer self-assembly (where v is the volume of the hydrophobic block, a_0 is the optimal surface area per head group, and L is the length of the hydrophobic block), continuously changes due to the increasing length of the core-forming block. These changes in the packing parameter are directly responsible for driving the observed morphological transitions. Armes' group also successfully monitored the PISA process during aqueous emulsion polymerization to synthesize amphiphilic block copolymers [33–35]. To facilitate in situ TR-SAXS measurements of emulsion polymerization, a bespoke cell designed for efficient stirring of the sample solution was utilized to ensure sample homogeneity and accurate scattering data acquisition.

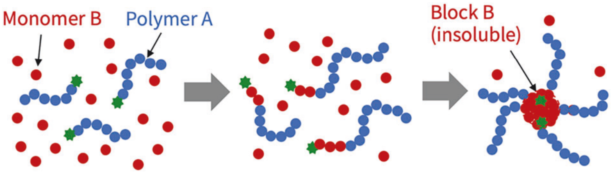

Fig. 4 Schematic illustration of PISA

The authors and coworkers also studied PISA by TR-SAXS, specifically focusing on spherical micelle formation [36]. A key insight from this study was the quantitative reproduction of TR-SAXS data. This was achieved by combining models of the polymerization reaction kinetics with micelle structure, assuming that micelle formation and growth (*via* unimer exchange and fusion) were sufficiently faster than the polymerization process. This rapid equilibration allowed the micelle system to remain in a thermodynamically stable state at each polymerization stage.

However, PISA systems often become kinetically trapped, particularly when the core-forming blocks exhibit glass transition temperatures (T_g) above the polymerization reaction temperature [37, 38]. This leads to the vitrification of the micellar core, arresting further structural evolution and preventing the structure from remaining thermodynamically stable. Consequently, T_g significantly influences PISA kinetics; while systems with T_g sufficiently below the polymerization temperature can be analyzed relatively easily (as demonstrated in ref. [36]), the complexity arising from vitrification is precisely what makes PISA kinetics so intriguing. A deeper understanding of

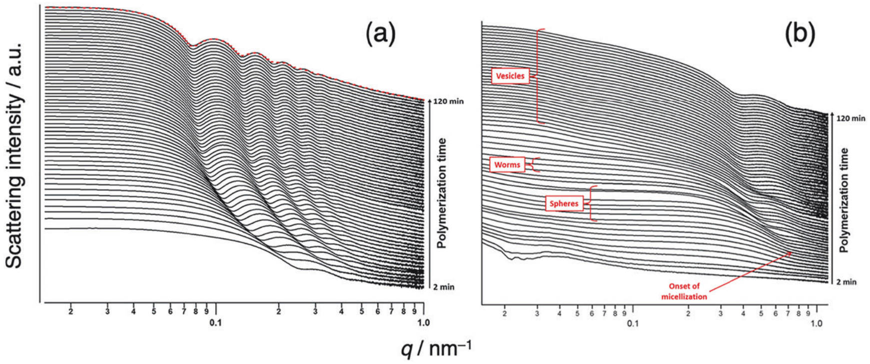

Fig. 5 SAXS profiles obtained in situ during PISA synthesis in spherical micelle case (**a**) and vesicle case (**b**). Reproduced from ref. [31]

these non-equilibrium dynamics during PISA could potentially lead to the preparation of metastable structures not achievable through conventional methods.

Another critical consideration in TR-SAXS studies of PISA is the radiation effect. X-ray irradiation of samples can generate radicals, which, in turn, can accelerate radical polymerization reactions during PISA [31, 32, 39]. This radiation-induced promotion of polymerization can significantly complicate the quantitative analysis of PISA. As the polymerization and self-assembly processes are already intricately coupled and simultaneously proceeding, time-resolved nuclear magnetic resonance (NMR) measurements are also important as well as TR-SAXS for understanding the PISA process. For example, by NMR measurements, the phenomenon where the polymerization rate increases at a certain time during PISA is often observed and it is attributed to the onset of self-assembly [40], as unreacted monomers become encapsulated within the nascent micelles. This local increase in monomer concentration and viscosity within the micellar core is believed to promote the polymerization rate. However, analyzing this monomer encapsulation behavior accurately by NMR and TR-SAXS without any radiation-induced artifacts remains challenging, as the promotion of polymerization by X-ray exposures almost always occurs, except at very low monomer concentrations (<1 wt%) [36].

To mitigate the radiation effect, Warren and coworkers utilized a continuous flow cell in conjunction with a laboratory SAXS instrument [41]. This setup allowed for a continuous supply of fresh reaction mixture to the X-ray beam, thereby minimizing the exposure time of any given volume of sample to the X-ray beam and consequently avoiding the promotion of the polymerization reaction. However, due to the inherent lack of high time resolution in their laboratory SAXS instrument, they were unable to precisely estimate the time point of the onset of self-assembly. In this context, TR-SANS offers a significant advantage. Neutron scattering, which leverages the de Broglie wave nature of neutrons, is typically performed with much lower energies compared to X-rays of the same wavelength. Consequently, neutron irradiation is far less likely to induce radical polymerization. For example, neutron irradiation at JRR-3 [42], at a wavelength 0.7 nm^{-1}, has been shown not to promote the radical polymerization of methyl methacrylate during TR-SANS measurements [43]. In addition, TR-SANS has tracked PISA of solvent-free systems *via* living anion polymerization [44, 45]. These studies suggest that TR-SANS is a highly beneficial technique for future studies aiming to accurately delineate the interplay between polymerization kinetics and self-assembly onset without radiation artifacts.

Beyond the forward process of PISA, exploring its reverse offers a unique opportunity for deeper insights into dynamic self-assembly. The field of depolymerization for polymers prepared *via* RAFT polymerization and atom transfer radical polymerization has seen rapid advancements recently [46]. The authors demonstrated that TR-SAXS could monitor the thermal depolymerization process of poly(benzyl methacrylate) (homopolymer) prepared thought RAFT polymerization [47]. This depolymerization proceeds *via* an unzipping mechanism, where monomers are successively released from the chain terminus. Unlike the significant artifacts often observed in TR-SAXS studies of the forward PISA process, no such artifacts were detected during this depolymerization study. This result suggests that TR-SAXS is a valuable tool for studying the depolymerization process, and, furthermore, the reverse process of PISA; i.e., “depolymerization-induced disassembly” of micelles.

Conclusion and outlook

TR-SAXS stands as an exceptionally powerful and versatile technique for unraveling the complex kinetic pathways governing block copolymer self-assembly in solution. Coupled with tools like stopped-flow mixers, it has enabled quantifying early-stage kinetics, resolving millisecond events, and revealing rapid nucleation and initial growth of nanostructures. Furthermore, it has allowed direct monitoring of morphological evolution, such as cylinder-to-sphere transitions, providing evidence for micellar shape changes and determining relative fractions of different morphologies and vesicle formation. TR-SAXS has also elucidated underlying mechanisms.

In PISA, TR-SAXS has been instrumental in observing in situ growth and morphological evolution during polymerization. While TR-SAXS offers significant progress, challenges persist regarding radiation effects and the intricate coupling of polymerization kinetics with self-assembly. However, complementary techniques like TR-SANS show promise in mitigating these issues. It is well known that TR-SANS utilizes different contrasts than SAXS, providing unique information unattainable by X-rays [8]. In addition to this feature, to monitor PISA processes, neutron radiation does not induce or promote polymerization, making TR-SANS particularly valuable for accurate quantitative analyses without interference.

A key illumination of TR-SAXS is that its data represents an average over the entire scattering volume. This can make it challenging to precisely analyze individual morphologies when multiple forms coexist during processes such as micelle-to-vesicle transitions [27]. To gain a more comprehensive understanding, combining TR-SAXS with liquid-phase transmission electron microscopy (LP-TEM) is also crucial. LP-TEM enables the observation of structural evolution at the single-particle level [29, 48], offering a complementary perspective to the ensemble-averaged TR-SAXS data.

The upcoming upgrade of the SPring-8 synchrotron radiation facility to SPring-8-II [49] exemplifies the global trend of new and upgraded synchrotron facilities [50], promising significant enhancements in X-ray brilliance and coherence. This will lead to superior time resolution, enabling the investigation of faster dynamic processes and transient phenomena. Moreover, the improved coherence will enable advanced techniques like X-ray photon correlation spectroscopy (XPCS), a powerful tool for probing dynamics across a wide range of length and time scales and providing unprecedented insights into complex systems. These synergistic advancements are profoundly significant for future research into the dynamics of self-assembly, poised to revolutionize our understanding of material self-organization and offer unparalleled opportunities for real-time investigations of kinetic pathways and structural evolution.

Finally, integrating experimental TR-SAXS data with advanced theoretical modeling and data analysis techniques and simulations is essential for predictive models of block copolymer self-assembly, enabling rational design of functional soft materials. Continued innovation in TR-SAXS methodologies, coupled with advancements in data analysis and theoretical understanding, promises to deepen our comprehension of block copolymer self-assembly, paving the way for novel materials in various applications.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

References

1. Bates FS, Fredrickson GH. Block copolymers—designer soft materials. Phys Today. 1999;52:32–38.
2. Hamley IW. Block copolymers in solution: fundamentals and applications. Chichester, England: John Wiley & Sons; 2005.
3. Mai Y, Eisenberg A. Self-assembly of block copolymers. Chem Soc Rev. 2012;41:5969–89.
4. Geng Y, Discher DE, Kaplan DL, Smith A, Yang Z. Polymer scaffolds for tissue engineering: applications in drug delivery and tissue repair. Adv Mater. 2001;13:1184–8.
5. Zhang L, Eisenberg A. Multiple morphologies of “Crew-Cut” aggregates of polystyrene-*b*-Poly(acrylic acid) block copolymers in aqueous solutions. Science. 1995;268:1728–31.
6. Lodge TP. Block copolymers: past, present, and future. Macromol Chem Phys. 2007;208:1083–95.
7. Matsen MW. Block copolymer thermodynamics. J Polym Sci Part B Polym Phys. 2002;40:1259–90.
8. Lund R, Willner L, Richter D. Kinetics of block copolymer micelles studied by small-angle scattering methods. Adv Polym Sci. 2013;259:51–158.
9. Lodge TP, Seitzinger CL, Seeger SC, Yang S, Gupta S, Dorfman KD. Dynamics and equilibration mechanisms in block copolymer particles. ACS Polym Au. 2022;2:397–416.
10. Narayanan T. Recent advances in synchrotron scattering methods for probing the structure and dynamics of colloids. Adv Colloid Interface Sci. 2024;325:103114.

11. Kresheck GC, Hamori E, Davenport G, Scheraga HA. Determination of the dissociation rate of dodecylpyridinium iodide micelles by a temperature-jump technique. J Am Chem Sci. 1966;88:246.
12. Lund R, Willner L, Monkenbusch M, Panine P, Narayanan T, Colmenero J, et al. Structural observation and kinetic pathway in the formation of polymeric micelles. Phys Rev Lett. 2009;102:188301.
13. Kalkowski J, Liu C, Leon-Plata P, Szymusiak M, Zhang P, Irving T, et al. In situ measurements of polymer micellization kinetics with millisecond temporal resolution. Macromolecules. 2019;52:3151–7.
14. Lund R, Wilner L, Richter D, Lindner P, Narayanan T. Kinetic pathway of the cylinder-to-sphere transition in block copolymer micelles observed in situ by time-resolved neutron and synchrotron scattering. ACS Macro Lett. 2013;2:1082–7.
15. Bungenberg de Jong HG. Colloid science, 2. Amsterdam: Elsevier Publishing; 1949, pp. 335–432.
16. Fuoss RM, Sadek H. Mutual interaction of polyelectrolytes. Science. 1949;110:552–4.
17. Takahashi R, Narayanan T, Sato T. Growth kinetics of polyelectrolyte complexes formed from oppositely-charged homopolymers studied by time-resolved ultra-small-angle X-ray scattering. J Phys Chem Lett. 2017;8:737–41.
18. Van Vaerenbergh P, Léonardon J, Sztucki M, Boesecke P, Gorini J, Claustre L, et al. An upgrade beamline for combined wide, small and ultra small-angle x-ray scattering at the ESRF. AIP Conf Proc. 2016;1741:030034.
19. Narayanan T, Sztucki M, Zinn T, Kieffer J, Homs-Puron A, Gorini J, et al. Performance of the time-resolved ultra-small-angle X-ray scattering beamline with the Extremely Brilliant Source. J Appl Cryst. 2022;55:98–111.
20. Amann M, Diget JS, Lyngsø J, Pedersen JS, Narayanan T, Lund R. Kinetic pathways for polyelectrolyte coacervate micelle formation revealed by time-resolved synchrotron SAXS. Macromolecules. 2019;52:8227–37.
21. Vogelaar TD, Torjusen H, Narayanan T, Lund R. The kinetic pathways for the formation of complex coacervate micelles of antimicrobial peptides and block copolymers. Macromolecules. 2025;58:158–68.
22. Vogelaar TD, Szostak SM, Lund R. Coacervation in slow motion: kinetics of complex micelle formation induced by the hydrolysis of an antibiotic prodrug. Mol Pharmaceutics. 2024;21:4157–68.
23. Wu H, Ting JM, Yu B, Jackson NE, Meng S, de Pablo JJ, et al. Spatiotemporal formation and growth kinetics of polyelectrolyte complex micelles with millisecond resolution. ACS Macro Lett. 2020;9:1674–80.
24. Takahashi R, Sato T, Terao K, Yusa S. Intermolecular interactions and self-assembly in aqueous solution of a mixture of anionic–neutral and cationic–neutral block copolymers. Macromolecules. 2015;48:7222–9.
25. Takahashi R, Sato T, Terao K, Yusa S. Reversible vesicle–spherical micelle transition in a polyion complex micellar system induced by changing the mixing ratio of copolymer components. Macromolecules. 2016;49:3091–9.
26. Takahashi R, Narayanan T, Yusa S, Sato T. Kinetics of morphological transition between cylindrical and spherical micelles in a mixture of anionic–neutral and cationic–neutral block copolymers studied by time-resolved SAXS and USAXS. Macromolecules. 2018;51:3654–62.
27. Takahashi R, Narayanan T, Yusa S, Sato T. Formation kinetics of polymer vesicles from spherical and cylindrical micelles bearing the polyelectrolyte complex core studied by time-resolved USAXS and SAXS. Macromolecules. 2022;55:684–95.
28. Weiss TM, Narayanan T, Wolf C, Gradzielski M, Panine P, Finet S, et al. Dynamics of the self-assembly of unilamellar vesicles. Phys Rev Lett. 2005;94:038303.
29. Ianiro A, Wu H, van Rijt MMJ, Vena MP, Keizer ADA, Esteves ACC, et al. Liquid–liquid phase separation during amphiphilic self-assembly. Nat Chem. 2019;11:320–8.
30. Marras AE, Ting JM, Stevens KC, Tirrell MV. Advances in the structural design of polyelectrolyte complex micelles. J Phys Chem B. 2021;125:7076–89.
31. Derry MJ, Fielding LA, Warren NJ, Mable CJ, Smith AJ, Mykhaylyk OO, et al. In situ small-angle X-ray scattering studies of sterically-stabilized diblock copolymer nanoparticles formed during polymerization-induced self-assembly in non-polar media. Chem Sci. 2016;7:5078–90.
32. Czajka A, Armes SP. In situ SAXS studies of a prototypical RAFT aqueous dispersion polymerization formulation: monitoring the evolution in copolymer morphology during polymerization-induced self-assembly. Chem Sci. 2020;11:11443–54.
33. Brotherton E, Hatton FL, Cockram AA, Derry MJ, Czajka A, Cornel EJ, et al. In situ small-angle X-ray scattering studies during reversible addition−fragmentation chain transfer aqueous emulsion polymerization. J Am Chem Soc. 2019;141:13664–75.
34. Czajka A, Armes SP. Time-resolved small-angle X-ray scattering studies during aqueous emulsion polymerization. J Am Chem Soc. 2021;143:1474–84.
35. Czajka A, Lovell PA, Armes SP. Time-resolved small-angle X-ray scattering studies during the aqueous emulsion polymerization of methyl methacrylate. Macromolecules. 2022;55:10188–96.
36. Takahashi R, Miwa S, Sobotta FH, Lee JH, Fujii S, Ohta N, et al. Unraveling the kinetics of the structural development during polymerization-induced self-assembly: decoupling the polymerization and the micelle structure. Polym Chem. 2020;11:1514–24.
37. Shibata I, Sugawara-Narutaki A, Takahashi R. Polymerization-induced self-assembly enables access to diverse highly ordered structures through kinetic and thermodynamic pathways. Chem Sci. 2025;16:7921–8.
38. Hou W, Yin X, Zhou Y, Zhou Z, Liu Z, Du J, et al. Kinetically controlled preparation of worm-like micelles with tunable diameter/length and structural stability. J Am Chem Soc. 2024;146:24094–104.
39. Yamanaka R, Sugawara-Narutaki A, Takahashi R. In situ monitoring of polymerization-induced self-assembly and gelation during the synthesis of triblock copolymers via time-resolved small-angle X-ray scattering and rheology. Macromolecules. 2023;56:4354–61.
40. Blanazs A, Madsen J, Battaglia G, Ryan AJ, Armes SP. Mechanistic insights for block copolymer morphologies: how do worms form vesicles? J Am Chem Soc. 2011;133:16581–7.
41. Guild JD, Knox ST, Burholt SB, Hilton EM, Terrill NJ, Schroeder SLM, et al. Continuous-flow laboratory SAXS for in situ determination of the impact of hydrophilic block length on spherical nano-object formation during polymerization-induced self-assembly. Macromolecules. 2023;56:6426–35.
42. Mayumi K, Geonzon L, Hashimoto K, Oda T. Hierarchical structure of soft materials studied at small-angle neutron scattering instrument, SANS-U. J Phys Soc Jpn. 2024;93:091007.
43. Suzuki Y, Doi Y, Misima R, Mayumi K, Matsumoto A. Heterogeneities at the onset of reaction acceleration during bulk polymerization of methyl methacrylate investigated by small-angle neutron scattering. Macromolecules. 2023;56:3731–8.
44. Yamauchi K, Hasegawa H, Hashimoto T, Tanaka H, Motokawa R, Koizumi S. Direct observation of polymerization-reaction-induced molecular self-assembling process: in-situ and real-time SANS measurements during living anionic polymerization of polyisoprene-block-polystyrene. Macromolecules. 2006;39:4531–9.
45. Motokawa R, Taniguchi T, Kumada T, Iida Y, Aoyagi S, Sasaki Y, et al. Photonic crystals fabricated by block copolymerization-induced microphase separation. Macromolecules. 2016;49:6041–9.
46. Jones GR, Wang HS, Parkatzidis K, Whitfield R, Truong NP, Anastasaki A. Reversed controlled polymerization (RCP):

depolymerization from well-defined polymers to monomers. J Am Chem Soc. 2023;145:9898–915.

47. Takahashi R, Sugawara-Narutaki A. Observing depolymerization of a RAFT polymer by time-resolved small-angle X ray scattering. ACS Polym Au. 2025;5:129–33.
48. Parent LR, Gnanasekaran K, Korpanty J, Gianneschi NC. 100th anniversary of macromolecular science viewpoint: polymeric materials by in situ liquid-phase transmission electron microscopy. ACS Macro Lett. 2021;10:14–38.
49. Watanabe T, Tanaka H. SPring-8 upgrade project: accelerator redesigned and restarted. Synchrotron Radiat N. 2023;36:3–6.
50. Taylor A. Facility updates: the bright future of synchrotron science. Synchrotron Radiat N. 2025;38:2–3.

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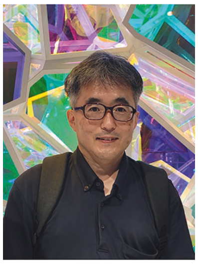

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