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Cyclic Polymers Leading *Topology Effects* upon Self-assemblies, Dynamics and Responses

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Abstract

A variety of single- and multicyclic polymers having programmed chemical structures with guaranteed purity have now become obtainable owing to a number of synthetic breakthroughs achieved in recent years. Accordingly, a broadening range of studies has been undertaken to gain updated insights on fundamental polymer properties of cyclic polymers in either solution or bulk, in either static or dynamic states, and in self-assemblies, leading to unusual properties and functions of polymer materials based on their cyclic topologies. In this article, we review recent challenges aiming for distinctive properties and functions by cyclic polymers unattainable by their linear or branched counterparts. We focus, in particular, on selected examples of unprecedented *topology effects* by cyclic polymers upon self-assemblies, dynamics and responses, to highlight current progress in *Topological Polymer Chemistry*.

1. Cyclic polymers and topology effects thereby

There are abundant examples where the form of objects directs their functions and properties under any dimensions and scales. In polymer chemistry and polymer materials science, on the other hand, the choice of macromolecular structures has mostly been limited to linear or randomly branched forms. During the recent decade in this century, however, a variety of precisely controlled polymer topologies has been constructed along with the introduction of intriguing synthetic techniques.[1] In particular, an important class of polymers having cyclic and multicyclic topologies has now become obtainable with unprecedented structural precision, and their qualities are now satisfactorily guaranteed by the newly introduced spectroscopic and chromatographic techniques, including MALDI-TOF mass, critical-condition HPLC.[2] The expansion of the choice of reliable polymer samples has now inspiring the modeling/simulation studies to reveal any topology effects, significantly benefited by the ongoing progress of computational techniques toward more and more complex and larger systems in rigorous manner.[3] These developments have also allowed to perform the experimental verification studies over classical or newly proposed theoretical models on fundamental static/dynamic properties uniquely achieved by cyclic and multicyclic polymers.[2,3] Moreover, conceptually novel challenges to realize unprecedented properties and functions simply based on the form, i.e. *topology*, of polymer molecules, and their eventual applications in polymer materials design have now become in practice.[2-4]

Cyclic biopolymers, frequently encountered in DNAs, peptides and polysaccharides, have long been attracted significant interests due to their sophisticated topology-based functions, and have been valuable resources for designing functions and properties in synthetic polymer materials.[5] Synthetic single cyclic (ring) polymers, in particular, have been studied theoretically as well as experimentally to understand fundamental properties of randomly coiled polymer molecules uniquely relied on their chain topology of either linear or cyclic form.[6] It has been shown that the hydrodynamic volume, i.e., 3D size, of ring polymers is distinctively smaller than the linear counterpart. Moreover, the diffusion properties are pronouncedly affected by the shape or topology of polymer molecules. Indeed, the diffusion process of linear/branched polymers is conformed to reptation mechanism with snake-like motion in which the chain ends are critical in their dynamics, but is distinctive to ring polymers in the absence the chain ends with speculatively amoeba-like motion.[7, 8]

It is also notable that the elimination of end groups by ring polymers from linear counterparts results in distinctive properties, as typically observed in the glass transition temperature

(Tg). The Tg of ring polymers is noticeably higher than that of linear polymers of identical molar mass, i.e. the chain length, while the distinction tends to diminish along with the increase of the polymer chain length. Hence, in a strict sense, this is regarded as a chain-length (or chain-end concentration) dependent property, and is contrastive to the intrinsic ones like the hydrodynamic volume, independent of the polymer chain length. Nevertheless, as the elimination of the chain ends of linear polymers inevitably transforms their topology into a ring form, either of intrinsic or chain-end concentration dependent properties could be referred as *topology effects*.[2]

While principal and fundamental properties of simple ring polymers are comprehensively addressed by seminal works during the early periods in polymer science dated back to middle of the precediung century,[6] a variety of homopolymers and copolymers of not only simple ring but also complex cyclic forms have now been purposely produced to investigate their *topology effects* in more comprehensive and rigorous manner. Recent works reporting diverse topology effects by cyclic polymers are collected in Table 1, classified into several sub-areas to cover the current scope of research activities. It is notable, in particular, that an increasing number of works are focusing on topology effects in a variety of self-assembly states, i.e., micelles/interfaces, complex/complexations, gels/gelation, etc (Table 1, A). This trend is reasoned by that any topology effects could be amplified in self-assembly states, even the linear/cyclic distinction in single polymer molecules is not obviously significant.[2]

Another area of persisting research interests includes topology effects upon dynamics and conformational properties of ring polymers, in contrast to their linear counterparts, covering the diffusion behaviors, crystallization kinetics, entanglemens, etc. (Table 1, B) Indeed, the increasing number of simulation/modelling studies have appeared in recent years, undoubtedly due to the enormous progress in computational and calculation technologies, and also inspired by new synthetic developments to afford appropriate polymer samples used for experimental verification studies. In turn, these new modelling/simulation works have been inducing further experimental studies toward the precision synthesis of new target polymers. Such extensive research efforts, in particular upon polymer dynamics are again reasoned by that the non-reptation mechanism unique for ring polymer dynamics is expected to create distinction against their liner polymer counterparts.

It is remarkable, moreover, that new approaches have appeared for topology effect by cyclic polymers by making use of adaptive polymer materials responding to either photonic, thermal, electronic or chemical stimuli under non-equilibrium conditions. (Table 1, C) Also in biomedical field, the topology effect by cyclic polymers against their conventional linear counterparts was exploited to achieve the controlled/improved bio-transportation as well as the gene/DNA delivery. (Table 1, D) Finally, cyclic polymers are now applied as structural scaffolds to construct nano-objects of unique non-linear forms, which will become a first step toward eventual nanotechnology. (Table 1, E)

We have reported various *topology effects* by cyclic and multicyclic polymers, obtainable through the precision synthesis protocols, including metathesis polymer cyclization (MPC)[9] as well as electrostatic self-assembly and covalent fixation (ESA–CF)[10] processes. In the following section, we show first *topology effects* by cyclic polymers upon self-assemblies, by using cyclic amphiphilic block copolymers to form micelles, in particular.[11-13] The elimination of chain ends in cyclic surfactants, forming the densely packed hydrophobic segment core and prohibiting the dynamic bridging between micelles, was found to cause the significant stabilization of micelles. In addition, the topology effect by linear and cyclic surfactants upon the stabilization of water/toluene emulsion was revealed.[14,15] The self-assembly of either linear or cyclic polymer surfactants at the toluene/water interfaces was considered to cause the amplified topology effect in their emulsion. Furthermore, linear and cyclic amphiphilic block copolymers having a liquid crystalline and hydrophobic segment were synthesized, and the topology effect was observed upon their self-assembly structure formation in comparison with their linear counterpart, and the subsequent electric field application causing the distinctive responses in their morphologies.[16]

In the next section, we discuss a set of linear and cyclic poly(THF)s consisting exclusively of monomer units, and of linear and cyclic stereoregular polylactide homo and block copolymers to examine the topology effect upon their crystallization kinetics and stereocomplex structures/properties.[17, 18] Furthermore, a cyclic polylactide incorporating a photo-cleavable unit is introduced for the photo-induced cyclic-linear topological transformation to cause the topology effect upon their thermal properties.[19]

In the final section, we show the single-molecule spectroscopic study to reveal the topology effect upon the polymer diffusion, by using a pair of linear and monocyclic as well as a set of 4-armed star and dicyclic (8-shaped) polymer samples prepared by the ESA-CF process, in which a fluorescent unit was commonly incorporated.[20] The newly developed spectroscopic technique was demonstrated to disclose the topology effect in diffusion process by the different polymer topology of either linear branched, single cyclic or dicyclic forms.[21-24]

2 *Topology effects* upon self-assemblies

2.1 Micelles by cyclic amphiphilic block copolymers

Self-assembly is a versatile process to construct functional nanostructures with the molecular-level precision, and micelles as well as vesicles made from surfactant molecules, including amphiphilic block copolymers, are typical examples with wide application possibilities.[25] Notably, in nature, a class of thermophilic archaea, single-cell microorganisms coping with hostile environments like high-temperature circumstances of hot springs and submarine volcanoes, have cyclic lipids as their cell membrane component.[26]

Inspired by this unique topology effect by the self-assembly of cyclic lipids exploited by the biosystem, we prepared a series of linear amphiphilic allyl-telechelic A-B-A type block copolymer having poly(*n*-butyl acrylate) (PBA) and poly(ethylene oxide) (PEO) segments, PBA-PEO-PBA and its cyclized PBA-PEO block copolymers by the MPC protocol (Fig. 1, (a) and (b), respectively).[27] The flower-like micelles were commonly formed by the self-assembly of linear or cyclic block copolymers with similar critical micelles concentrations (Fig. 1, (c) and (d), respectively).

A remarkable topology effect was disclosed on the micelles stabilization by a cyclized block copolymer against its linear counterpart, as a result of amplification of the topology effect by self-assemblies.[11,12] Upon the cloud points (T_c) measurements, the linear polymer micelles were observed to turn into turbid at 24–27 °C (Fig. 1, (e), while the cyclic counterparts were stable up to as high as 71–74 °C (Fig. 1, (f)). Therefore, the linear to cyclic transformation of the topology of polymer surfactant resulted in the drastic improvement in the thermal stability of micelles, despite the chemical structures and molecular weights are unaltered. Furthermore, the T_c was systematically tuned by using a series of micelles prepared by simply mixing the cyclic block copolymer and the linear precursor at various compositions (Fig. 1, (g)).

In addition, a pair of linear and cyclic amphiphilic block copolymers having poly(methyl acrylate) (PMA) as the hydrophobic segment were prepared with PEO as the hydrophilic counterpart, and micelles therefrom were subjected to compare their salt stability.[12] As an example, the micelle by the cyclic PMA-PEO surfactants was stable up to as high as 270 mg/mL of the NaCl concentration, in contrast to the linear PEO-PMA-PEO micelles precipitated only at 10 mg/mL of NaCl. Accordingly, the cyclic polymer micelles were proven to be stable not only against higher temperature but also higher salt concentration. Moreover, the T_c of micelles was systematically controlled in the wide temperature and salt concentration ranges by simply adjusting the mixing ratio of the cyclic and linear amphiphiles.[11] By taking advantage of this topology effect, a unique micellar catalysis was developed for a halogen exchange reaction.[12] The catalytic reaction using the cyclic amphiphile was accelerated by 50% in comparison with the relevant process with the linear counterpart catalyst (Fig. 1, (h).[12]

The higher stability of the micelles by the A-B type cyclic PBA-PEO against the A-B-A type linear counterparts was further elucidated by the X-ray structural analysis in solution.[13] It was shown, in particular, that the density of the hydrophobic PBA core was significantly higher for the cyclic polymer micelles (d = 1.06–1.23 g/cm^3), against the linear counterpart (0.93–1.08 g/cm^3). The density of the core of the cyclic polymer micelles was comparable to that of the bulk PBA (d = 1.08 g/cm^3), to accord with the absence of the chain ends and thus free volumes thereby for the cyclic polymer surfactant.

And for the flower-like micelles by the linear block copolymer surfactant, one of the chain ends could jump out from the core of the micelle, and cause the bridging between micelles after the dehydration. Consequently, the linear block copolymer micelles could result in the agglomeration at relatively low temperature, in contrast to the thermally robust cyclic counterpart, in which the bridging motion is unlikely to proceed due to its absence of the chain ends.[11]

2.2 Emulsion stabilization by cyclic amphiphilic block copolymers

The emulsion stabilization by polymer surfactants has routinely been employed in diverse applications, including the coating formation, the pharmaceutics/cosmetic formulation, the food processing, the detergents preparation, etc.[28] Hence, cyclic polymer surfactants will become a potentially attractive emulsion modifier, since both cyclic and linear polymer surfactants are chemically identical and are considered inherently compatible each other.

We prepared cyclic polystyrene (PS)-PEO block copolymers by making use of the MPC procedure with a linear block copolymer precursor, PS-PEO-PS, having olefinic end groups (Fig. 2, (a) and (b), respectively).[29] A pair of the A-B-A type linear and the A-B type cyclic block copolymer surfactants were subjected to the emulsion stabilization measurement, as the linear PS-PEO block copolymers have so far employed in the relevant studies on their self-assemblies, like micelles, vesicles and other complex aggregates,[30] and in particular, on the formation of simple to complex emulsion structures by the toluene/water system.[31]

The macroscopic phase separation of water–toluene emulsions was monitored by the presence of either the linear PS–PEO–PS or the cyclized PS–PEO surfactants.[15] Thus, a prescribed amount of the linear or cyclic polymer surfactant was dissolved in toluene (10 mL), and the solution was introduced in a 30-mL graduated glass cylinder. A series of volumes (5, 10 or 15 mL) of distilled water was then slowly added to form a two-phase solution. The graduated cylinder was vigorously agitated to give an emulsified solution and placed in a thermostated water bath at either 25, 50 or 75 °C. The phase separation process of the emulsified layer in the water phase, i.e., an oil-in-water emulsion was subsequently monitored (Fig 2, (c), (d) and (e), respectively). The phase separation was, as anticipated, quicker at higher temperature and faster by reducing the amount of water. At the same time, the phase separation kinetics was noticeably affected by the type of surfactants, and was significantly faster for emulsions containing the cyclic surfactant, particularly for toluene/water (10 mL/5 mL) at 75 °C (linear, ■; cyclic, □ in Fig 2, (c)), toluene/water (10 mL/10 mL) at 50 °C (linear, ▲; cyclic, △ in Fig 2, (d)), and toluene/water (10 mL/15 mL) at 25 °C (linear, ●; cyclic, ○ in Fig 2, (e)).

In the present emulsion system, the phase separation presumably proceeded through the coalescence of the oil droplets, promoted by the mass transfer of the block copolymer surfactants, initially located at the interface of the water/toluene phase.[15] And they tend to translocate gradually into the oil droplet phase as both PS and PEO segments of the surfactant molecule are soluble in toluene. During this process, the linear surfactant is expected to cause the bridging between the oil droplets with the extended chain conformation. Consequently, the coalescence of the oil droplets involved the translocation of the hydrophobic PS segments of the linear surfactants passing across the water phase between oil droplets, in contrast to the case with cyclic surfactants, where the mass transfer proceeds simply upon the dehydration. Accordingly, the bridging process undergoing exclusively by the linear surfactants could suppress the merging of the oil droplets, and the eventual phase separation. As in the stabilization of the micelles by cyclized block copolymers, the topology effect on the present emulsion stabilization is ascribed to the bridging by the surfactant having hydrophobic end segments, but this motion is inherently suppressed for the cyclic counterpart.

2.3 Self-assemblies by cyclic amphiphilic block copolymers having a liquid crystalline segment and their response behaviors

Liquid crystalline (LC) polymers have been extensively studied as they are able to respond to an electric or magnetic field owing to the rigidity and dielectric anisotropy of the polymer chain.[32] We prepared a pair of linear and cyclized amphiphilic copolymers having a hydrophilic poly(acrylic acid) segment (AA_m), combined with a common main-chain LC polymer component of poly(3-methylpentamethylene-4,4'-bibenzoate) (BB_n) (Fig 3, (a) and (b), respectively).[33] The topology effect upon their self-assemblies and, moreover, on their electric or magnetic field-responses was investigated accordingly.[16]

First, the solid state morphology of the linear and the cyclized block copolymers of different compositions was studied by small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD). Linear $AA_{21}BB_9AA_{21}$ (Fig 3, (c)), cyclic $AA_{33}BB_{10}$ (Fig 3, (d)), and cyclic $AA_{51}BB_{18}$ (Fig 3, (e)) formed lamellar microdomains, where only the BB_n segment of cyclic $AA_{51}BB_{18}$ gave a smectic CA phase (Fig 3, (e)). In contrast, linear $AA_{44}BB_9AA_{44}$ (Fig 3, (f)) and cyclic $AA_{100}BB_9$ (Fig 3, (g)) formed cylindrical microdomains. Furthermore, these amphiphilic block copolymers were self-assembled in water to form cylindrical micelles or vesicles, depending on the polymer concentration of the initial THF solution (Fig 4, (a) and (b), respectively). By the application of an electric field, the vesicles formed from linear $AA_{25}BB_{14}AA_{25}$ and cyclic $AA_{51}BB_{18}$ turned into substantially larger aggregates, presumably due to the reorganization of the LC segment in the bilayer (Fig 4, (c) and (d), respectively).

3. *Topology effects* upon crystallization

3.1. Crystallization kinetics by a *defect-free* cyclic poly(THF)

A class of ring polymers consisting exclusively of the monomer unit, in which not only chemically but also geometrically irregular, chain-end or branched structures are completely eliminated, are considered *defect-free*, and important for the rigorous examination of the fundamental properties of randomly coiled long-chain ring polymers, in comparison with their linear counterparts, both in solution and in bulk.[17]

Thus, we prepared a ring poly(THF) having a linking structure of a 2-butenoxy group, through the MPC process with a uniform-size, telechelic poly(THF) having allyl end groups.[9] Remarkably, the subsequent hydrogenation reaction of this linking group is capable of produce an oxytetrametylene group, identical to the monomer unit. By making use of this procedure, we prepared a series of *defect-free* ring poly(THF)s having different molecular weights, and their relevant linear counterpart, whose structure corresponds to one formed through the bond-breaking at the middle position of butane (tetramethylene) unit of the ring polymer and the subsequent addition of two hydrogen atoms.[17] We compared subsequently the isothermal crystallization kinetics of these model polymers, since the distinctive polymer topology effect is anticipated for the ring polymer against the linear counterpart.

Remarkable ring topology effects were revealed in the spherulite growth rates and spherulite morphologies in comparison with the relevant linear counterpart. Thus, the crystallization rate was slower for the cyclic poly(THF), and the unusual spherulites structure was formed.[17,34] The slower growth rate for the cyclic polymer was accounted for by their conformational constrain suppressing the propagation at the crystallization front. Interestingly, the faster crystallization rate was observed for cyclic poly(ε-caprolactone) in comparison with the linear counterpart,[35] and the faster diffusion of the cyclic polymers against the linear counterparts was postulated critical in this topology effect.

3.2 *S*tereocomplex by cyclic stereoregular polylactides

The stereocomplex formation process by a pair of complementary polymer components of either cyclic or linear form is expected to direct the complexation kinetics, the complex structures and their eventual stabilization, by reflecting the presence/absence of the conformational constraint by cyclic/linear polymer components, and to cause the subsequent topology effect. Polylactides are known as a typical example forming stereocomplexes by the combination of polymers having opposite stereoregularities.[36] Thus, a series of cyclic poly(L-lactide), PLLA, and poly(D-lactide), PDLA, as well as linear and cyclic stereoblock polylactides were systematically prepared through the click linking of telechelic polymer precursors having either azide or alkyne groups at the designated chain end of polylactides, and having also allyl groups at another chain end. They were subsequently cyclized by the MPC protocol to give the corresponding cyclic PLAs of opposite segment orientations.[18]

The homocrystals and stereocomplexes obtained by these linear and cyclic polylactides were first studied by WAXD as well as SAXS technique, and subsequently the melting point (T_m) measurements were performed to observe the topology effect upon the stereocomplex structures by the linear and the cyclic streroregualar homopolymers and block copolymers. Moreover, a pair of cyclic PLLA and PDLA, having an *o*-nitrobenzyl group as a photocleavable linker unit, were prepared (Fig 5, (a) and (b), respectively).[19] Thus, the cyclic polymer topology could be transformed into the linear form by the UV irradiation causing the chain cleavage reaction at the single prescribed location, while the molecular weight and the polymer chain structure remain intact. This photo-responsive topological conversion could resul in the simultaneous rearrangement of the stereocomplex structures. Thus, the T_m of the stereocomplex by the linear PLLA/PDLA was observed at 209 °C against that by the cyclic PLLA/PDLA at 167 °C before the UV irradiation. The distinction of as large as 40 °C between these T_m values corresponds to the lamellae thickness of the crystalline phase (l_c) with the extended chain conformation by the linear polylactide in contrast to the folded conformation by the cyclic counterpart (Fig 5, (c) and (d), respectively). Upon the UV irradiation of cyclic PLLA and PDLA having a photocleavable linker unit in solution, the T_m of the recovered product increased up to 211 °C, to accord with the topological transformation of polylactides from the cyclic to the linear form.

4. ***Topology effects*** upon diffusion by cyclic and dicyclic polymers revealed by single molecule spectroscopy

The diffusion process of linear or branched polymer molecules is conformed to a reptation mechanism, in which polymer molecules are allowed to undergo the snake-like motion, and their chain ends are critically important in their dynamics.[7] On the other hand, ring polymers in the absence the chain ends are distinctive to linear counterparts in their diffusion process, yet to be fully addressed, and an alternativer topology-directed mechanism like the amoeba-like motion is postulated.[8] In order to gain insights in the diffusion mechanism of cyclic polymers, a single-molecular fluorescent spectroscopy has now been developed.[37,38] In contrast to traditional experimental methods to characterize diffusive and relaxation dynamics of polymers with ensemble average, the single-molecule imaging is used to reveal the heterogeneities of polymer dynamics. As unconventional and complicated chain dynamics and interactions are assumed to operate in cyclic and multicyclic polymers, single-molecule approaches should become a powerful means for investigating their dynamics, as shown in the case of linear and cyclic DNAs.[22]

Thus, we prepared first a pair of linear and monocyclic poly(THF)s having a perylene diimide by the ESA–CF protocol, to introduce it either at the centre position of the linear or at the prescribed inner position of the cyclic polymer samples. Each polymer sample was then mixed in a linear poly(THF) matrix at the semidilute or in bulk conditions under extremely high dilution of 32–35 ppb. The diffusion process of the single molecules was monitored and analysed by a single-molecule localization and tracking method. Thus, the locations of the molecules in each image frame were precisely determined by two-dimensional Gaussian fitting, and the diffusion coefficients of individual molecules (D) were determined by mean-squared displacement (MSD) analysis of the trajectories. Finally, the D distributions were determined and compared with theoretical probability distributions.[21, 23]

Remarkably, a unimodal distribution of D was revealed for the linear polymer system, in contrast to a bimodal distribution for the cyclic counterpart. This distinction was reasoned by that a part of the cyclic polymers were threaded with the linear matrix polymers leading to the slower diffusion, while ones without threading were faster than the average diffusion of the linear polymers. Such topology effects upon the diffusion dynamics, often undetectable through the ensemble average techniques, are uniquely disclosed by means of the single-molecular spectroscopy technique.[21, 23]

Moreover, a pair of 8-shaped and four-armed star-shaped polymers were prepared also by the ESA–CF process, in which a perylene diimide fluorophore unit was purposely introduced at the core of the 8-shaped and four-armed star-shaped polymer structures (Fig 6, (a) and (b), respectively).[20] This pair of a perylene diimide-labelled, 8-shaped and four-armed star-shaped poly(THF)s was then mixed with a linear poly(THF) matrix to form a melt state at elevated temperatures, and was subjected to the single-molecular fluorescent spectroscopy.

The obtained frequency histograms of D values for 8-shaped and four-armed star-shaped polymers, calculated by the MSD analysis of the diffusion trajectories are listed in Fig 6, (c) and (d), respectively.[24] The mean D value of the 8-shaped polymers in the melt state (D = 0.156 $\mu m^2 s^{-1}$)

was comparable to that of the monocyclic polymer ($D = 0.155$ μm^{2}s^{-1}) with a similar ring size. On the other hand, multi-armed star polymers have D values depending on the number of arms. Notably, moreover, the slower diffusing component found for the 8-shaped polymers ($D = 0.061$ μm^{2}s^{-1}) was much smaller than that for the four-armed star polymer ($D = 0.133$ μm^{2}s^{-1}) although the total chain length in the 8-shaped polymers was similar to that in the four-armed star polymer. These results coincided with a simulation study, which predicted the slower diffusion of cyclic chains by the threading with linear chains, as was shown in the monocyclic and linear polymers. As the total chain length in the four-armed star-shaped polymer and the 8-shaped polymers was comparable, the faster diffusion observed for the latter should correspond to the suppression of the threading and/or the contracted dicyclic conformation.

4 Concluding remarks

Cyclic polymers have been considered as a material of great potential, and we have observed important developments in recent years on the efficient and innovative synthetic processes, and on the new purification and characterization techniques. Thereby a variety of single- and multicyclic polymers having programmed chemical structures with guaranteed qualities have now become obtainable. By taking advantage of these significant progress, unprecedented opportunities have now been realized to disclose unusual polymer properties by cyclic polymers, in either solution or bulk, in either static or dynamic states, and in self-assemblies, ready for the eventual applications. Topology effects are considered as a unique means to control polymer properties, in which no excessive change in molecular weights or chemical structures are involved, and thus any precaution over chemical toxicity or environmental pollution are not additionally required. Thus, one could apply the topology effect in polymer material design in order to purposely improve any properties of conventional polymeric materials. Moreover, any topology effects by cyclic polymers are to be exploited in tuning of a wide range of sophisticated functions based on dynamic physicochemical systems, as in a typical example of soft stimuli-responsive polymer materials.[39] Also in future, a variety of topology effects by not only simple ring polymers but also by multicyclic polymers[40, 41] are anticipated to be disclosed, and to be applied in practice for the routine methodology of polymer materials designs.

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Table 1. Recent reports on topology effects by cyclic polymers

Topology effect	Polymer type [a)]	Preparation method [b)]	Ref
A. Self-assemblies			
1. Micelles and emulsions	PEO-polyacrylate, PS-PEO block	End-linking (MPC)	11, 12, 15, 16
	Poly(NCA)	Ring-expansion (NHC)	42
	PCL-PS-der block with PEO graft	End-linking (ATRP-click)	43
	Polyacrylate-PAA block	End-linking (ATRP-click)	44
	PEO-PCL block	End-linking (click)	45
	Poly(glycidyl ethers), dicyclic, etc	End-linking (click)	46
	PS-PAA, dicyclic block	End-linking (click)	47
	Simulation	n.a.	48
2. Stereocomplexes	PLA	Ring-expansion (NHC)	49
	PMMA	End-linking (click)	50
	PLA	MPC	18, 19
3. Gels	Poly(cyclooctene)-der	Ring-expansion (REMP)	51
	PS, Polysiloxane, PEO	End-linking (amidation)	52, 53
	Poly(NCA) copolymer	Ring-expansion (NHC)	54
	Poly(alkylene phosphate)	Ring-expansion (NHC)	55
4. Bulk properties (melting, glass transition,	Polyester (lactones)	Ring-expansion (NHC)	56

phase spacing, etc)	PS and deuterated PS	End-linking (MPC)	57
	Poly(NCA)	Ring-expansion (NHC)	54
	PS-PEO block copolymer	End-linking (click)	58
	PS, multicyclics	End-linking (click)	59
B. Dynamics/Conformations			
1. Diffusion	Poly(THF), cyclic and dicyclic	End-linking (ESA-CF)	21, 23, 24
	PS and deuterated PS	End-linking (living PS)	60, 61
	Simulation	n.a.	62, 63
2. Crystallization kinetics	Poly(THF)	End-linking (ESA-CF)	64
	PE	Ring-expansion (REMP)	65
	PCL	End-linking (click)	66
	Poly(NCA)-der	Ring-expansion (NHC)	67
3. Rheology/Entanglement	PS, PEO, Polyisoprene	End-linking (living precursors)	63
	Simulation	n.a.	68, 69
4. Blends/composites	PS and POSS or C60	End-linking (click)	70
	PCL and CNT	End-linking (click)	71
5. Conformations	PS	End-linking (living PS)	72

	Amylose Simulations	enzymatic n.a.	73 62, 63, 74-89
C. Responses			
1. Photo responses	PS-der PMMA-der Polythiophene	End-linking (living PS) End-linking (ATRP-click) End-linking (condensation)	90 91, 92 93
2. Thermo/chemoresponses	Poly(aldehyde)	Ring-expansion (cationic)	94-96
3. Topological transformation	PEO PS PS	Reversible (metal coordination) Reversible (H-bonding) Reversible (metal coordination)	97 98 99
D. Bioconjugates			
1. Biotransportation	PAA-der-PEG graft Oligopeptides	End-linking (ATRP-click) End-linking (S-S bonding)	100 101
2. Gene/DNA delivery	PMMA-der (cationic) Polyethylene imine	End-linking (ATRP-click) End-linking (click)	102 103

E. Nanoobjects			
1. Nanostructures	Poly(norbornene)-der	Ring-expansion (REMP)	104
2. Nanostructures(metalated)	Poly(norbornene)-der	Ring-expansion (REMP)	105

a) PEO: poly(ethylene oxide) or polyethylene glycol, PS: polystyrene, poly(NCA): poly(*N*-carboxyanhydride), PCL: poly(ε-caprolacxtone), PAA: poly(acrylic acid), PMMA: poly(methyl methacrylate), PLA: poly(lactic acid), poly(THF): poly(tetrahydrofuran), PE: polyethylene

b) MPC: metathesis polymer cyclization, ATRP: atom-transfer radical polymerization, REMP: ring-expansion metathesis polymerization, ESA-CF: electrostatic self-assembly and covalent fixation.

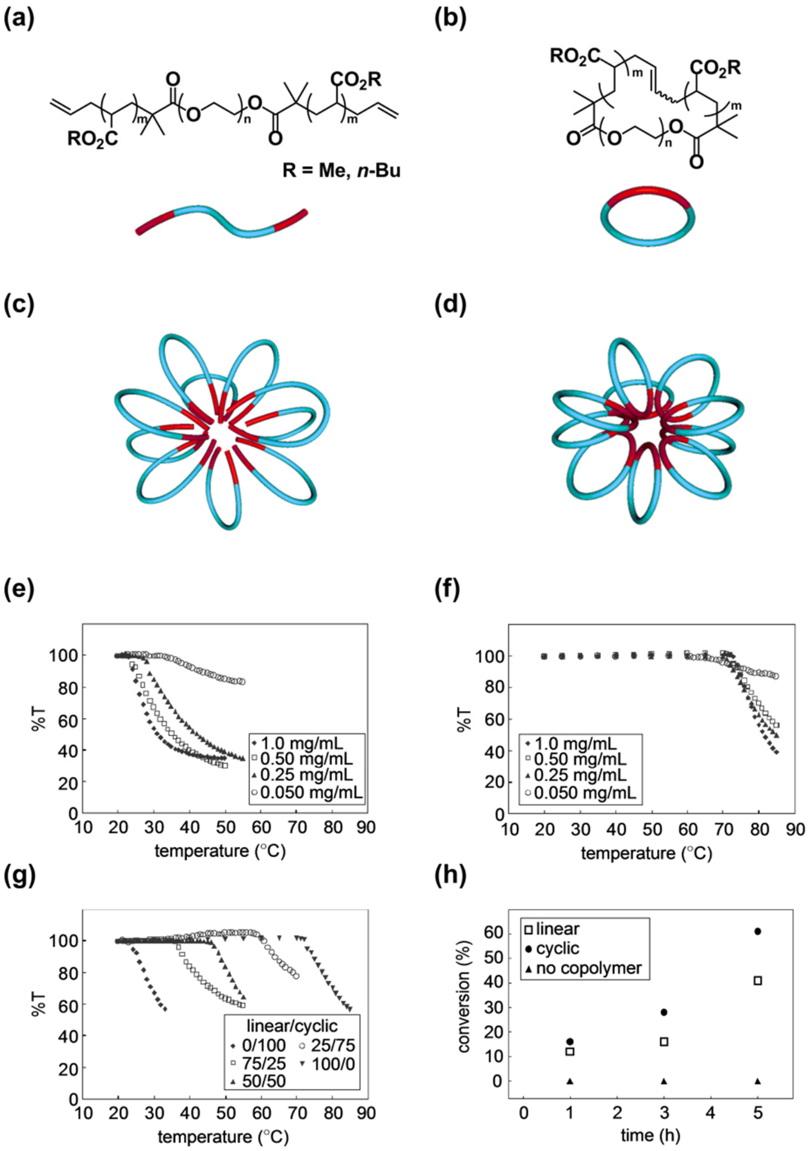


Fig. 1. Chemical structures of (a) linear and (b) cyclic amphiphilic block copolymers. Schematic representation of a (c) linear polymer micelle and (d) cyclic polymer micelle. Temperature-dependent transparency (%T) of micellar solutions of (e) linear, (f) cyclic, and (g) mixture of the linear and cyclic amphiphilic block copolymers. (h) Time-dependent conversion of the halogen exchange reaction. Reproduced from ref. 11, Copyright 2010 American Chemical Society, and from ref. 12, Copyright 2013 Nature Publishing Group.

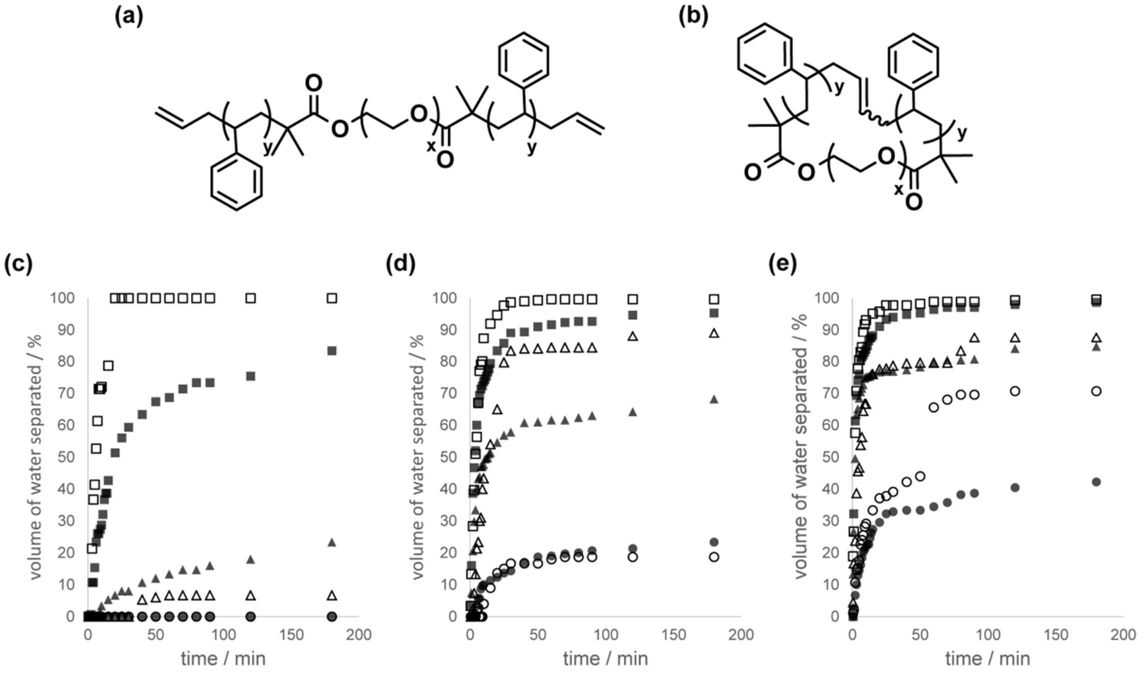


Fig. 2. Chemical structures of (a) allyl-telechelic PS–PEO–PS and (b) cyclized PS–PEO surfactants. Time-dependent volume fraction of the separated water layer from the water phase of the emulsion, in the presence of linear PS–PEO–PS (■, ▲, ●) and cyclized PS–PEO (□, △, ○) with a surfactant concentration of 0.1 g/L in toluene at a toluene/water ratio of (c) 10 mL/5 mL, (d) 10 mL/10 mL, or (e) 10 mL/15 mL at 25 °C (●, ○), 50 °C (▲, △), or 75 °C (■, □). Reproduced from ref. 15, Copyright 2015 Nature Publishing Group.

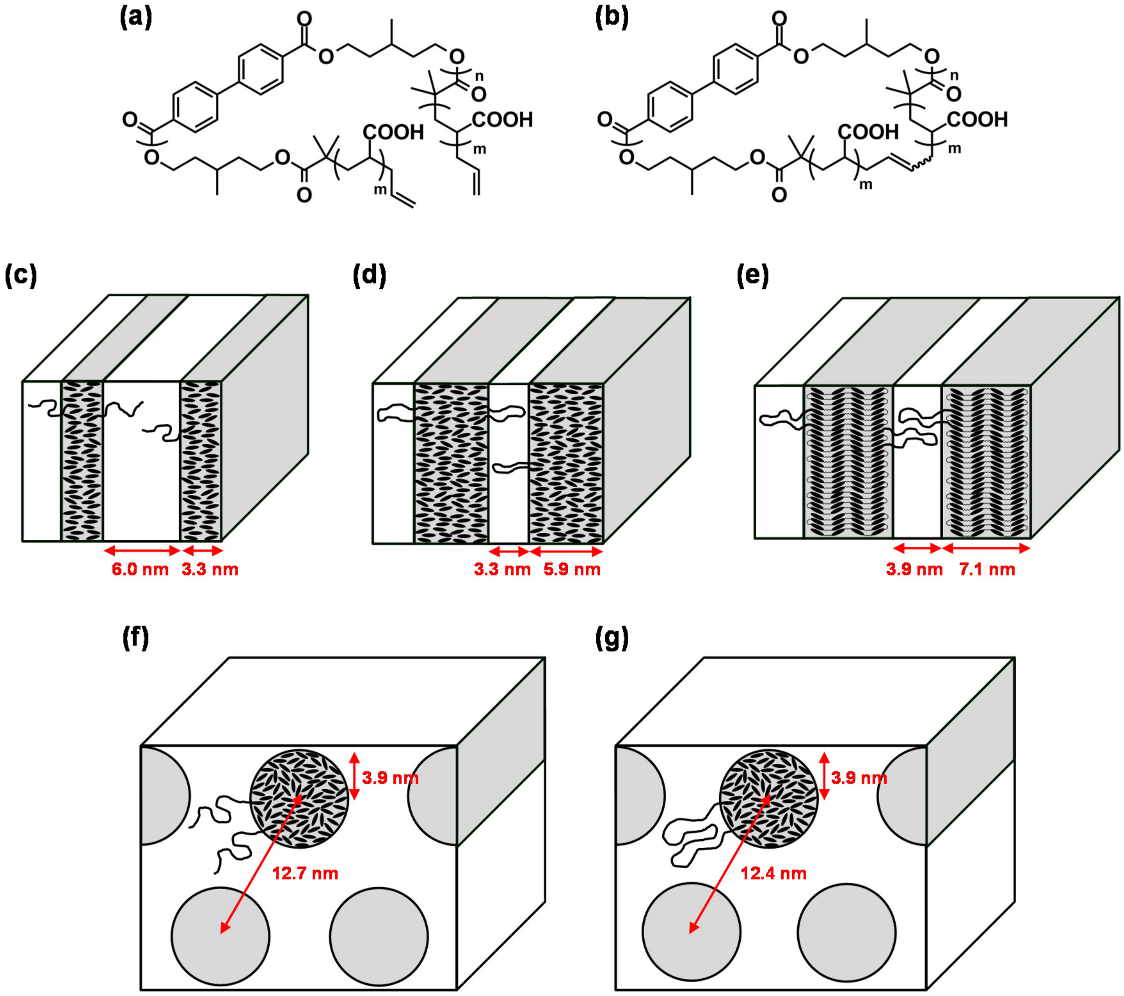


Fig. 3. Chemical structures of (a) linear $AA_mBB_nAA_m$ and (b) cyclic $AA_{2m}BB_n$. Schematic illustration for the phase separation models of (c) linear $AA_{21}BB_9AA_{21}$, (d) cyclic $AA_{33}BB_{10}$, (e) cyclic $AA_{51}BB_{18}$, (f) linear $AA_{44}BB_9AA_{44}$, and (g) cyclic $AA_{100}BB_9$. Reproduced from ref. 16, Copyright 2015 Royal Society of Chemistry.

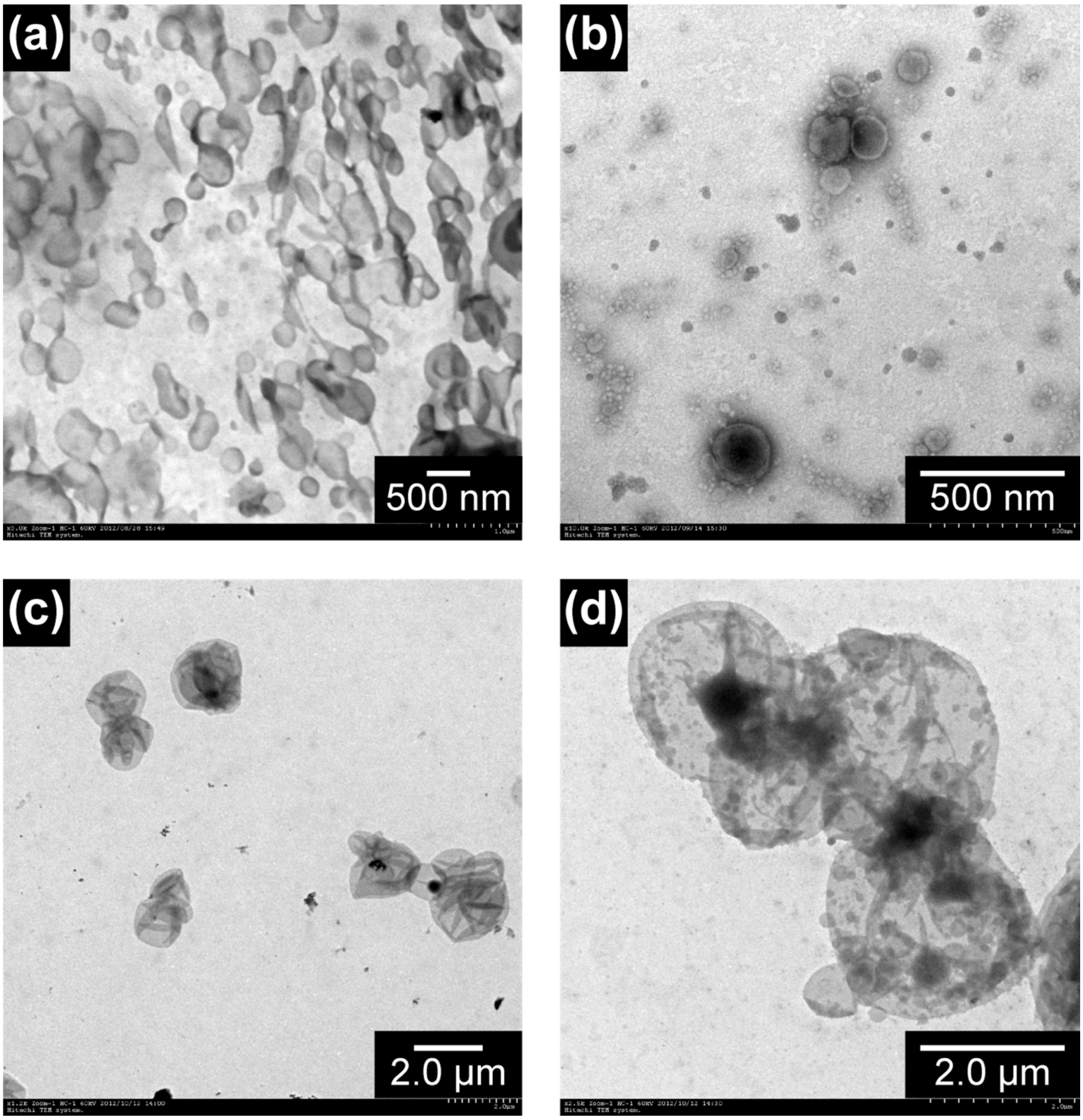


Fig. 4. TEM images of self-assembled structures from linear $AA_{25}BB_{14}AA_{25}$ and cyclic $AA_{51}BB_{18}$ using an initial THF solution with a polymer concentration 10 mg/mL before and after applying an electric field (*E*) of 1.5 V/mm for 2 min. (a) Linear, before *E*, stained with TI-blue. (b) Cyclic, before *E*, stained with TI-blue. (c) Linear, after *E*. (d) Cyclic, after *E*. Reproduced from ref. 16, Copyright 2015 Royal Society of Chemistry.

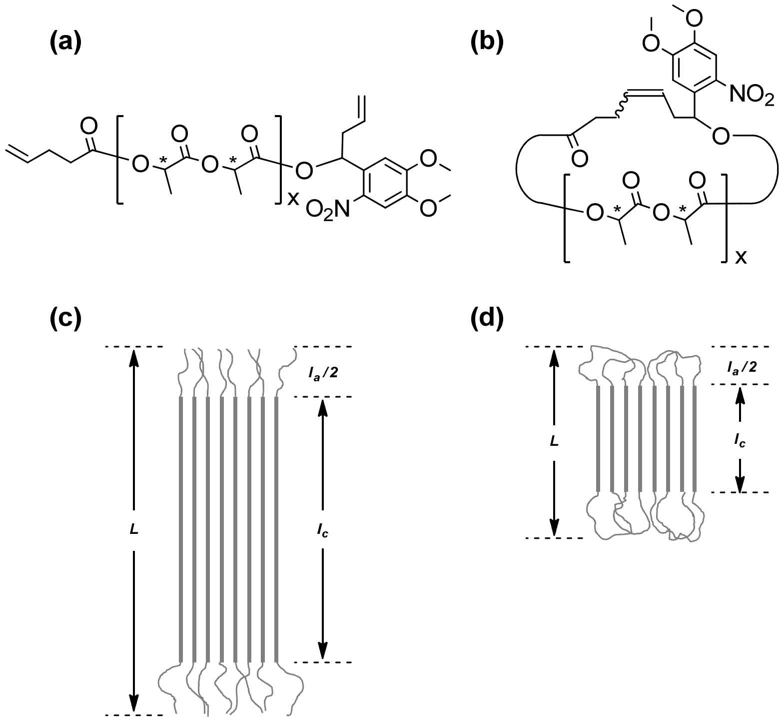
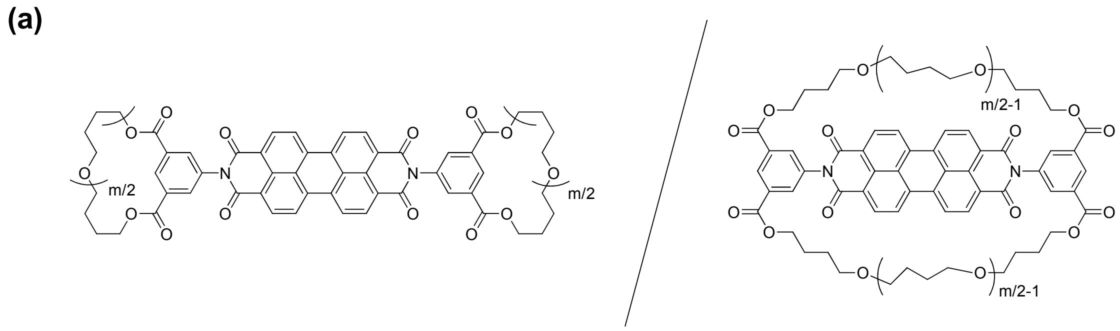
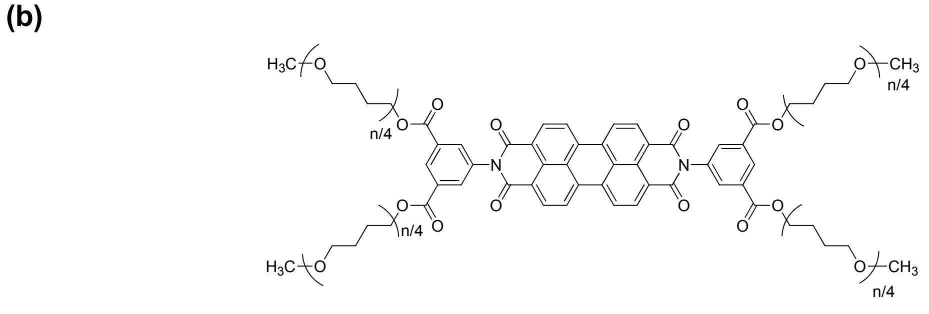


Fig. 5. Chemical structures of photocleavable (a) linear and (b) cyclized polylactide. Schematic illustrations of the lamellar structures of (c) linear and (d) cyclized homocrystals and stereocomplexes of the photocleavable polylactides. *L*, long period; I_{a}, amorphous thickness; I_{c}, crystal thickness. Reproduced from ref. 19, Copyright 2015 Royal Society of Chemistry.



8-shaped poly(tetrahydrofuran)



four-armed star-shaped poly(tetrahydrofuran)

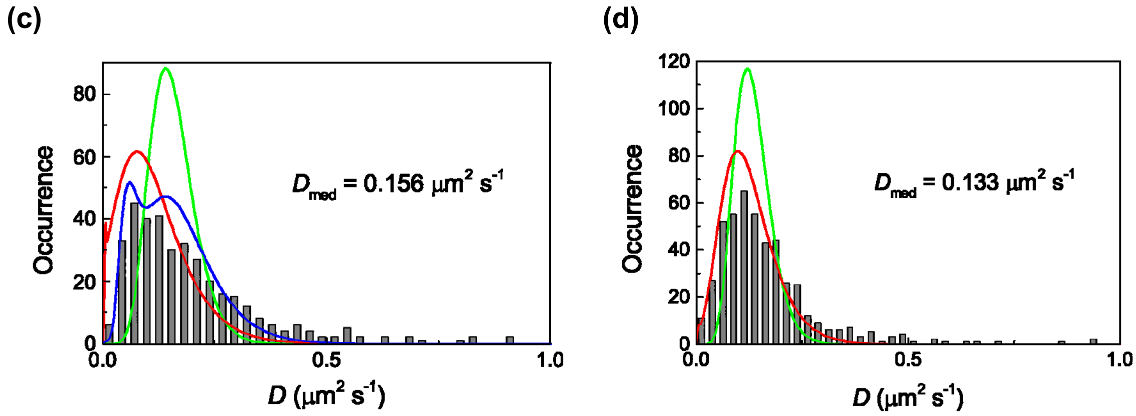


Fig 6. Chemical structures of (a) 8-shaped and (b) four-armed star-shaped poly(THF) incorporating a perylene diimide unit. Frequency histograms (grey bars) of the diffusion coefficient calculated for (c) 8-shaped and (d) four-armed star-shaped polymers in a linear poly(THF) matrix. The green, red, and blue lines indicate homogeneous diffusion models, single Gaussian models, and double Gaussian models, respectively. Reproduced from ref. 24, Copyright 2015 Royal Society of Chemistry.

A Table of Contents Entry

Cyclic Polymers Leading *Topology Effects* upon Self-assemblies, Dynamics and Responses

Takuya Yamamoto* and Yasuyuki Tezuka*

Cyclic polymers have disclosed unprecedented topology effects upon their self-assemblies, dynamics and responses.