Polymer Chemistry

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Cite this: *Polym. Chem.*, 2017, **8**, 5845

Characterizing single chain nanoparticles (SCNPs): a critical survey†

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Received 30th July 2017,
Accepted 25th August 2017

DOI: 10.1039/c7py01278k

rsc.li/polymers

We provide the results of a critical literature survey on the reported sizes of single chain polymer nanoparticles (SCNPs), an emerging class of functional nanomaterials with sub-30 nm diameters. Comparing different size evaluation techniques (DLS, 2D DOSY NMR, viscometry as well as microscopic techniques) by plotting the SCNPs' estimated diameters, *D*, *versus* their measured (apparent) number average molecular weight, M_n, we demonstrate the vast data scatter that besets their analysis. We show that while relative reductions in measured diameter certainly indicate chain collapse, accurately describing the absolute size of SCNPs in solution remains a challenging task. Critically, conformation-size relationships emerge depending on the method used for size determination. We submit that the vast majority of reported sizes are only indicative of the relative size reduction during chain collapse and that absolute size determination approaches currently in use need to be further refined.

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The field of single chain polymer nanoparticles (SCNPs)[1–6] (occasionally also referred to as nanogels) has seen substantial growth over the last 15 years based on a plethora of experimental techniques becoming available for the synthesis of well-defined functional precursor macromolecules, most prominently reversible deactivation radical polymerization (RDRP)[7,8] in combination with versatile modular ligation processes. SCNPs are intramolecular, cross-linked single polymer chains whose properties are distinctly different from their linear parent polymers. In contrast to cyclic polymers containing exactly one connection,[9,10] the properties of SCNPs are not exclusively dominated by the absence of free chain ends, but by both the nature and quantity of intramolecular crosslinks.

The ultimate aim of synthetic SCNP design is to achieve full molecular control over the morphology and folding behavior of the precursor chains, ideally mimicking the functionality and precision of naturally occurring biomolecules.[11] Clearly, although impressive progress has been made over the last decade, this aim remains largely elusive.

One of the major challenges in the field is the characterization of the obtained nanoparticles, which can be beset with problems reaching from their molecular characterization, their mass determination and a reliable morphological assessment. Chemically, nuclear magnetic resonance (NMR) spectroscopy as well as – most recently – high resolution mass spectrometry[12] are employed, while size – or rather the changes in size – is typically assessed *via* size exclusion chromatography (SEC) coupled to viscometry and MALS detectors, dynamic light scattering (DLS) and, less frequently, pulse field gradient NMR methods such as 2D DOSY.[3] In certain cases, atomic force microscopy (AFM) as well as transmission electron microscopy (TEM) has been employed, too. Critically, a set of the obtained size values (most from DLS and SEC measurements) has been used in a pioneering assessment by Pomposo and colleagues to derive information on SCNP shape and the expected size reduction upon intrachain collapse in both reversible and irreversible collapse scenarios.[13,14] By invoking Flory-theory arguments, a functioning relation was suggested that – within experimental error limits – predicts the experimentally observed relative collapses well. Interestingly, and

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† Electronic supplementary information (ESI) available: A detailed table containing number average molecular weights, M_n, sizes, as well as the techniques employed for the characterization of the SCNPs and the details for the calculation of protein D_h values can be found in this section. See DOI: 10.1039/c7py01278k

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perhaps not surprisingly, most studies focus on discussing the relative changes that occur in coil dimensions when going from the non-crosslinked precursor to the compact SCNP state. However, the absolute values of the obtained sizes are typically not discussed. The reason for this lack of a discussion of the absolute sizes is connected to the lack of information that is to be expected in terms of the final size of the SCNPs, which varies as a function of the employed solvent as well as the number of cross-linking points – as quantified by Pomposo and colleagues – yet also depends on the prepolymer, type of cross-linking chemistry and the specifically employed reaction conditions. In the current contribution, we provide a concise overview of the thus far reported sizes of SCNPs as obtained *via* DLS,[15–49] DOSY,[18,19,21,50] SEC coupled to a viscometry detector[51–58] as well as microscopy[44,45,47,50] and comment on the observed numbers. It is hoped that the summary of sizes and their visualization provided herein will aid the community in further understanding SCNP folding and lead to improved protocols for size determination.

In our survey of the literature available data on the size of the obtained SCNPs (denoted as the diameter, D, assessed *via* viscometry, AFM, TEM and DOSY as well as DLS based on the Stokes–Einstein relation), we have made the following observations, which will be discussed and evaluated in detail in the following: (i) The molecular weights of the precursor polymers ranges from as small as 2000 Da to over 200 kDa, constituting a very wide spread of number average molecular weights. However, caution is advised when discussing these molecular weights, as only in cases where the precursor chain exclusively consists of (functional) polystyrenes or poly(methyl methacrylates) and the analysis is based on polystyrene or poly(methyl methacrylate) SEC calibration, these numbers are beset with a small error. Due to many SCNPs having a non-polystyrene or non-PMMA based backbone, relative changes in size are almost exclusively discussed as the primary methodology to demonstrate the intra-molecular folding of linear polymers into SCNPs. In some cases absolute molecular weight methods are employed to determine the precursor size, yet most studies report relative molecular weights. (ii) For (apparent) identical molecular weights, there exists a wide spread of observed sizes for the SCNPs. For example, for a molecular weight of close to 25 kDa, the literature indicates D values that range from 7.4 nm (in a polyether system with a functionalization degree of 18% using thiol–yne cross-linking chemistry)[56] to 17.8 nm (in a polycyclooctadiene system cross-linked with 1 mol% rhodium chloride complexation)[30] or, even more pronounced for 50 kDa from 6.8 nm (in a poly (methyl methacrylate) system consisting of nominally 26% eneamine cross-links)[29] to 19.8 nm (in a poly(acrylate) system with 9% complementary hydrogen bonding *via* UPy moieties).[24] Similar spreads can be found for lower molecular weights, too. For example, for an apparent molecular weight of close to 15 kDa, values ranging from 3.8 to 8.0 nm have been reported (in a poly(azobenzene) ADMET polymer with nominally 50% NITEC cross-linking[19] *vs.* a polystyrene system with exactly two complementary hydrogen bonding cross-links),[22] and even for 10 kDa spreads from above 1 to 4.4 nm are literature known.[21,23] While some variation is expected in terms of the different folding chemistries employed, the coil dynamics and the number of established cross-links, this variation is indeed remarkable. Although estimations of the SCNPs density based on assumptions should be treated with strong caution as it requires knowledge of the particles shape and a highly reliable value for both D_h and the number average molecular weight, high D_h values generally indicate a very loosely packed particle. For example, based on spherical particles, densities of approx. 0.01 g cm^{-3} are estimated in some cases (*e.g.*, D_h 17.8, M_n 25 kDa),[30] which is 14 times less dense than a well-solvated poly(styrene) chain of similar M_n in cyclohexane, which features a D_h of close to 8.2 nm (density approximately 0.14 g cm^{-3}).[60] While such a distinct difference in SCNP density will be affected by inaccuracies of the apparent M_n as previously discussed in (i), inaccuracies of the D_h have a more drastic effect on the density as r is raised to the power of 3. (iii) When going to lower molecular weight systems, below 20 kDa, the reported apparent D_h values in some cases appear too small, leading to densities that exceed those of the bulk material. Clearly, measuring reliable D values in such size regimes is extremely challenging, yet some of these values have been confirmed with DOSY measurements[19,21,50] and even TEM[47,50] in some systems suggesting highly compact particles, as also noted by Pomposo and colleagues.[35,59] In any case, apparently too strong reductions in size do not appear to be uncommon.

To visualize these observations, we have constructed a graph which combines a large number of literature reported DLS (black), SEC viscometry (red), DOSY (blue) and microscopy (green) data by plotting the obtained D values *vs.* the (apparent) molecular weights (M_n). D refers to the diameters measured from the different techniques, *i.e.*, D_h (DLS and DOSY), equivalent sphere diameter (viscosity) or the visually relevant geometrical diameter (microscopy). Due to the low polydispersity of most of the reported functional polymers employed for the preparation of SCNPs, we consider that the difference between M_n and M_w is negligible. Fig. 1 depicts the above noted spread very well, while – not surprisingly – a general trend towards smaller D values with decreasing molecular weight is evident.

It is an interesting exercise to plot constant density lines into Fig. 1 to arrive at Fig. 2a. Here, we plotted the theoretical D_h as a function of M_n for constant density values using a simplistic solid sphere model. As an upper limit, we selected a density of 1.4 g cm^{-3} as some proteins have been reported to reach such densities.[61,62] To further compare the SCNPs with their natural analogs, we calculated the D_h for a general data set spanning more than 37 000 different proteins from their experimentally determined R_g values and plotted against M_n (Fig. 2b and c).[63] This set of protein data displays a relatively well-defined border of D_h values towards an M_n dependent maximum density threshold. Especially in the M_n regime >100 kDa, this maximum density aligns very well with the

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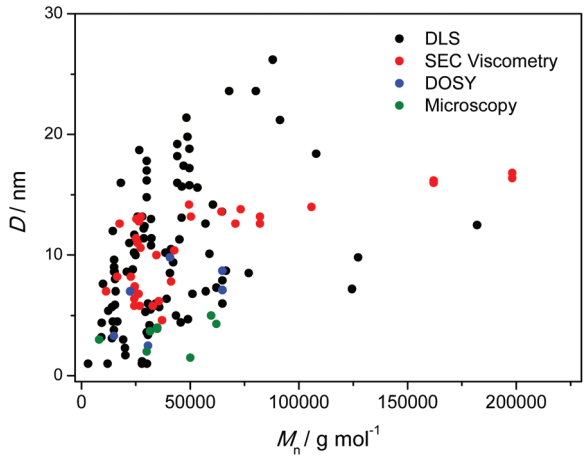

Fig. 1 *D vs.* the (apparent) M_n of reported SCNPs (for the full collation of all data points within the figure, refer to Table S1 in the ESI†).

solid sphere model of a constant density of 1.4 g cm^{-3}, while protein densities far exceeding even 1.4 g cm^{-3} are observed for low molecular weights. Some studies have indeed argued that ideal SCNPs should be as closely packed as the corresponding bulk material (approx. 1 g cm^{-3} or even slightly above) and provide experimental evidence for this notion.[35] However, densities exceeding its corresponding bulk material and the extensive protein envelope appear to be physically inaccessible. To address the question of where the low density limit for an SCNP lies, which can still be termed as SCNP, we take reference from one of our earlier studies, where we estimate the D_h of open and closed configurations of a simple polystyrene folding system merely tethered at its chain ends *via* all atomistic molecular dynamics simulations (violet dot, Fig. 2b and c).[64] On the basis of a folded circular 5 kDa polystyrene chain, a density of 0.3 g cm^{-3} is approximated, providing a hint that higher order cross-linked true SCNP structures should feature densities well in excess of 0.3 g cm^{-3}. Nevertheless, we also include constant density functions for 0.1 as well as 0.5 g cm^{-3}, which we suggest as minimum SCNP density in Fig. 2a–c. Inspection of these plots makes it immediately evident that – based on densities between 0.5 and 1 g cm^{-3} – a very high number of SCNP systems are below the density threshold of 0.5 g cm^{-3} and even below the density of linear polystyrene in a good solvent[65] (pink dots, Fig. 2b and

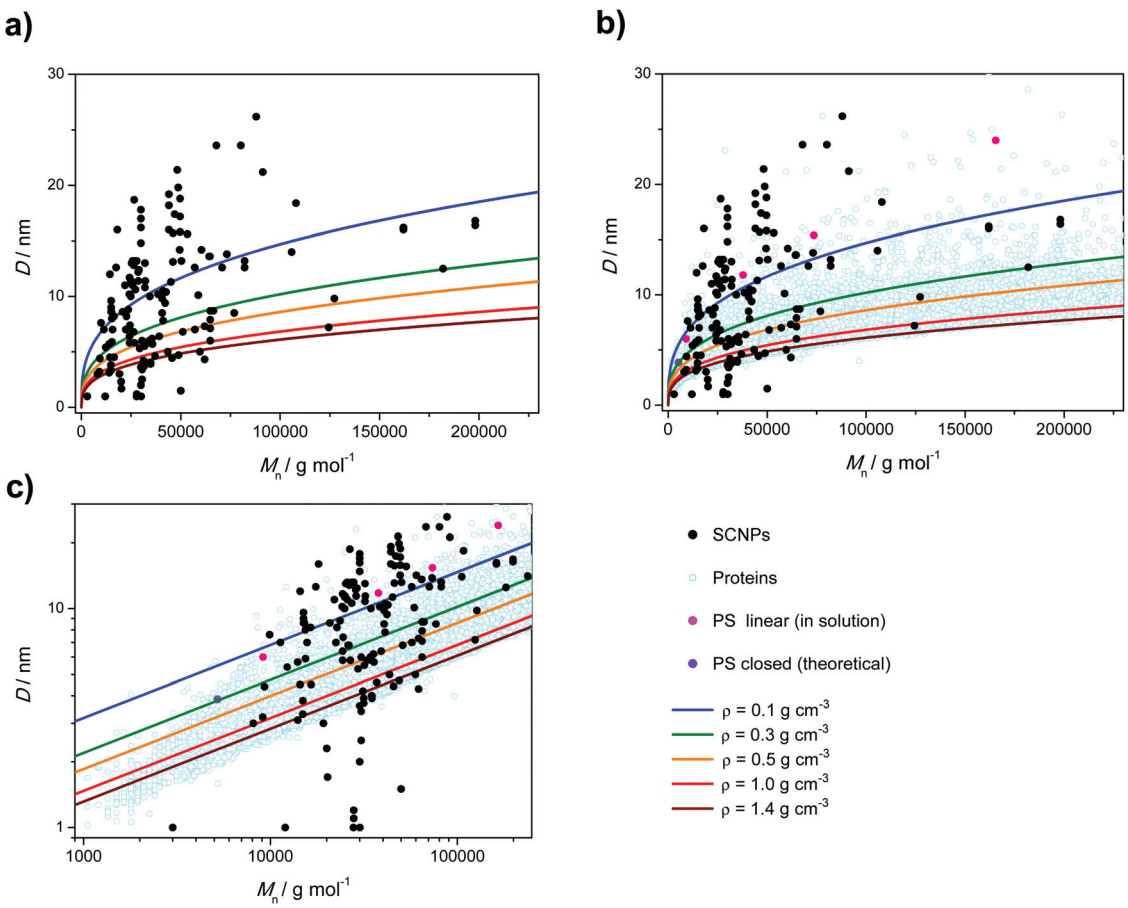

Fig. 2 (a) *D* (from all surveyed methods) *vs.* (apparent) M_n of the reported SCNPs including density functions; (b) *D vs.* (apparent) M_n of the reported SCNPs including D_h values of 37 000 different proteins (light blue circles),[63] linear polystyrene in a good solvent (pink dots)[65] and theoretical D_h for 5 kDa polystyrene in a closed conformation (violet dot);[64] (c) *D vs.* (apparent) M_n of the reported SCNPs (log–log plot).

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c). In contrast, a few systems show apparent densities that exceed the 1.4 g cm^{-3} upper limit and some of the results lie outside the possible conformational space exceeding the density of proteins of comparable molar masses (Fig. 2b and c). Since no apparent patterns seemed to emerge with regard to an 'allowed' SCNP density envelope, we explored individual plots based on the employed characterization method (Fig. 3). Inspection of DLS (Fig. 3a) and viscometric based data (Fig. 3b) yields surprising results. Perhaps the most startling observation is the lack of trends observed in the expected densities of the SCNPs when measured with DLS. In fact, more measurements lie outside the expected density realm than lie within it (14 too dense, 42 too loose and 32 within the envelope), even if we allow for densities down to 0.1 g cm^{-3} to be counted as SCNPs, which is an unlikely assertion. It should be noted that similar to calculating M_n *via* comparison to a given standard, DLS also invokes critical assumptions, *i.e.* that all SCNPs are hard spheres in solution and it does not take into account the conformation of the measured objects. This assumption only allows for the calculation of R_h (and in turn D_h) based on the Stokes–Einstein relation and neglects the radius of gyration (R_g) of a polymer in solution thus leaving the true nature of the SCNPs' size incomplete (refer also to the ESI†). Furthermore, strong scattering of large particles can suppress the detection of smaller particles, which is a major problem when number distributions are to be derived. In order to obtain reliable data for a wide range of sizes, angle dependent dynamic light scattering should be a viable option. Thus, for very small macromolecules, the data should be taken cautiously. The Pomposo team have made remarkable strides addressing this issue by incorporating SAXS and SANS techniques in their characterization repertoire.[66–69]

Interestingly and outside the SCNP field, a recent study on cyclic polyenes reports a D_h of 4.4 nm for an M_n of 45.6 kDa, corresponding to a nominal density of 1.67 g cm^{-3}.[70] For the linear counterpart, a D_h of 5.2 nm (M_n = 47.3 kDa) was reported, which still suggests a nominal density of 1.09 g cm^{-3}. Thus, here and in the SCNP field, it remains to be established what the exact cause of these apparently too compact – and as noted above too loose – structures is, ranging from DLS measurements beset with a large error, molecular weight determinations with considerable uncertainties or – in the case of very low densities – a possible ineffectiveness of the crosslinking process. However, it is important to point out that in all systems where the collapse is covalently driven, size exclusion chromatography measurements unambiguously confirm the collapse of the precursor chain.

Viscometric measurements are an interesting alternative and do not rely on the assumptions made in DLS. Interestingly, size data derived from viscometry – mainly

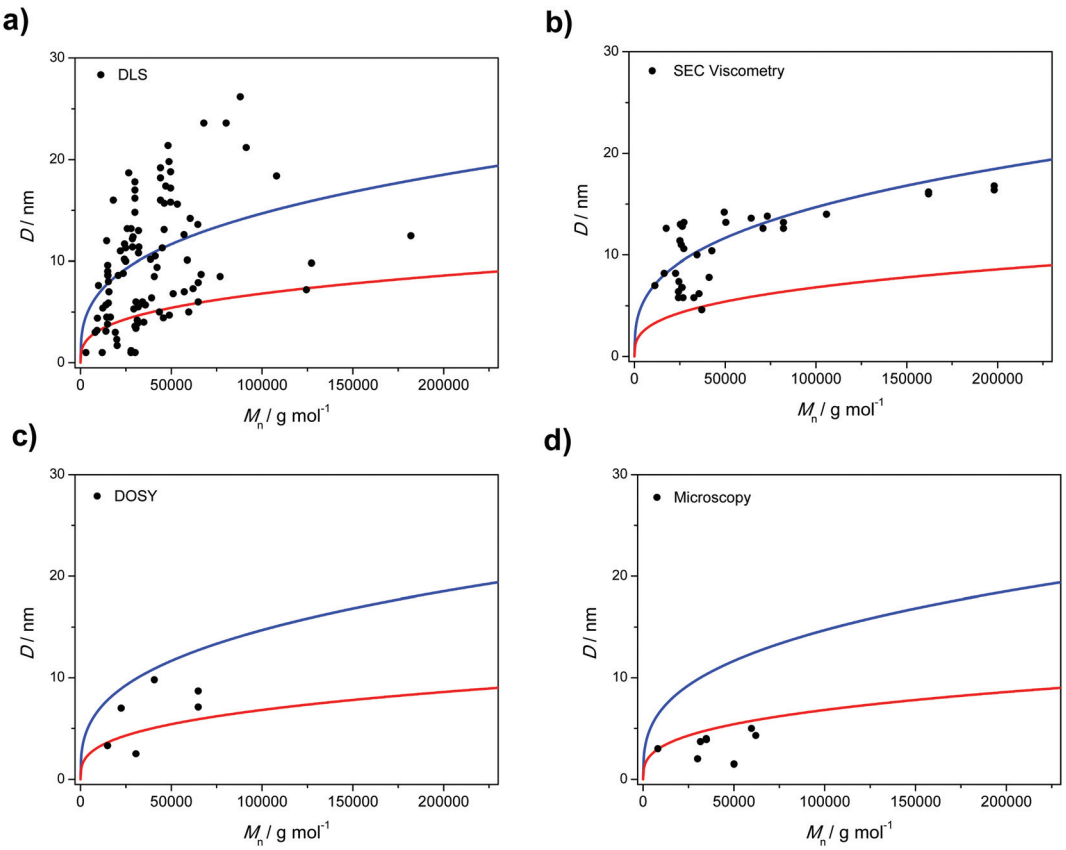

Fig. 3 Diameter (D) *vs.* (apparent) M_n of SCNPs measured by (a) DLS; (b) viscometry; (c) 2D DOSY-NMR and (d) microscopy. The blue line indicates a density of 0.1 g cm^{-3} and the red line 1 g cm^{-3}.

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reported by the Berda team – seem to follow the allowable density realm more closely up to 200 kDa. However, calculating a D *via* viscometry requires knowledge of a particular polymer's behavior within a specific solvent in order to yield its intrinsic viscosity, which in essence is the inverse density function of the polymeric material ([mL g^{-1}]) in solution. D can be calculated *via* the Einstein–Simha relation *via* $V_\eta = M[\eta]/(2.5N_A)$ and $D_\eta = 2\ (3V_h/4\pi)$, where $[\eta]$ is intrinsic viscosity, M the molar mass, V_η the equivalent sphere radius[71] (in some reports equally treated as V_h) volume and N_A Avogadro's constant. Note that the prerequisite of knowing the materials density in order to deduce D could be the reason that the viscometric size measurements for the SCNPs follow the expected density trends to a much closer degree. The contrast between these two characterization methods is indeed remarkable, however, one must be cautious when using the viscometric examples as the number of SCNPs fully characterized with viscometry are much fewer than those characterized *via* DLS. Further examples will need to be characterized *via* viscometry in order to assess if the true D of SCNPs is best measured *via* viscometry.

The limited number of examples measured with DOSY and microscopy makes it difficult to draw final conclusions from their stand-alone plots (Fig. 3c and d). Although examples exist of D values measured *via* microscopy techniques in the expected size regime, these numbers cannot be directly compared with D_h as D_h, by definition, is a measurement of a polymer in solution. Due to the fact that AFM and TEM are generally devoid of solvent and drop casted onto surfaces (cryo-TEM being one exception), the observed sizes can be expected to deviating by some degree. Nevertheless, the small sizes reported by microscopic methods are remarkable, all falling below the high density limit.

In summary, a careful survey and analysis of the SCNP literature and the size data contained therein has revealed interesting and important aspects on how SCNPs are currently characterized. Outside of the methods that provide chemical characterization, the approaches available for characterizing SCNPs rely on various techniques assessing their absolute size, yet most studies are concerned with changes in size only. Here, we provide an analysis of the absolute sizes as they relate to their apparent M_n and estimate the potential implications for the apparent density of these particles. We demonstrate that if only DLS and relative M_n are reviewed, a complex picture with a wide spread of absolute sizes emerges. However, we have also evaluated the literature findings on SCNP sizes based on viscometry, DOSY and microscopic methods. This analysis appears to suggest that techniques evaluating the SCNP's intrinsic viscosity may provide the most reliable results. While we can certainly not offer a conclusive answer for the observed absolute size behavior, we submit that the careful analysis provided herein is critical for moving the field towards not only relative size change observations and their rationalization, but also absolute radii discussions, which are critical for the design of functional biomimetic entities.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

C. B.-K. acknowledges support from the Queensland University of Technology (QUT), the Australian Research Council (ARC) in the context of a Laureate Fellowship as well as continued support from the Karlsruhe Institute of Technology (KIT) *via* the STN and BIFTM programs of the Helmholtz association. In addition, support from the SFB 1176 funded by the German Research Council (DFG) in the context of projects A1 and A2 is gratefully acknowledged. H. F. acknowledges generous funding from the German National Academy of Sciences Leopoldina. Prof. Dr Manfred Schmidt (University of Mainz) is thanked for interesting discussions regarding particle densities. Kilian Wüst (KIT/UNSW) is acknowledged for carefully commenting on the final version of the manuscript. In addition, the authors thank all the PhD and postdoctoral researchers in the QUT/KIT SCNP sub-group.

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