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Tuning the Properties of Hydrogen-bonded Block Copolymer Worm Gels Prepared via Polymerization-Induced Self-Assembly

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Polymerization-induced self-assembly (PISA) is exploited to design hydrogen-bonded poly(stearyl methacrylate)-poly(benzyl methacrylate) [PSMA-PBzMA] worm gels in n-dodecane. Using a carboxylic acid-based RAFT agent facilitates hydrogen bonding between neighboring worms to produce much stronger physical gels than those prepared using the analogous methyl ester-based RAFT agent. Moreover, tuning the proportion of these two types of end-groups on the PSMA chains enables the storage modulus (G') of the 20% w/w worm gel to be tuned from ~4.5 kPa up to ~114 kPa. This is achieved via two complementary routes: (i) an in situ approach using binary mixtures of acid- and ester-capped PSMA stabilizer chains during PISA or (ii) a post-polymerization processing strategy using a thermally-induced worm-to-sphere transition to mix acid- and ester-functionalized spheres at 110 °C that fuse to form worms on cooling to 20°C. SAXS and rheology studies of these hydrogen-bonded worm gels provide detailed insights into their inter-worm interactions and physical behavior, respectively. In the case of the carboxylic acid-functionalized worms, SAXS provides direct evidence for additional inter-worm interactions, while rheological studies confirm both a significant reduction in critical gelation concentration (from approximately 10% w/w to 2-3% w/w) and a substantial increase in critical gelation temperature (from 41 °C to 92 °C). It is remarkable that a rather subtle change in the chemical structure results in such improvements in gel strength, gelation efficiency and gel cohesion.

Introduction

Hydrogen bonding is widely regarded as the most important example of a non-covalent interaction between molecules. Indeed, hydrogen bonding is an essential component of the secondary structure of DNA via formation of complementary base pairs. This well-known phenomenon has been exploited in polymer science by various research groups to generate supramolecular morphologies, as well as to tune mechanical properties. For example, 2-ureido-4(1H)-pyrimidone (UPy) motifs have been used to introduce highly cooperative hydrogen bonding interactions in either aqueous or non-aqueous media. Thus, Meijer and co-workers prepared poly(ethylene glycol)-based hydrogels by introducing UPy groups into amphiphilic copolymers in order to form strong hydrogen bonds that act as physical cross-links. Leibler’s group reported the design of hydrogen-bonded synthetic rubbers using renewable starting materials that exhibit both self-healing and thermoreversible behavior. Kornfield and co-workers utilized charge-assisted hydrogen bonding to design complementary low molecular weight telechelic precursors that self-assemble to form high molecular weight ‘megasupramolecules’ in non-polar media. This approach confers a significant thickening effect, while irreversible shear-induced degradation can be avoided via a ‘self-healing’ mechanism. Hence these hydrogen-bonded nanostructures significantly out-perform high molecular weight polysisobutylene additives as anti-misting agents for jet fuel. Similar hydrogen bonding interactions between imidazole and carboxylic acid groups have been exploited for the formation of hydrogels with enhanced mechanical properties, while Ikkala and co-workers reported exquisite control over multiple length scales via hydrogen bonding-mediated self-assembly of a 1:1 methanesulfonic acid/poly(4-vinylpyridine) using varying amounts of pentadecylphenol. The discovery of living anionic polymerization, and more recently the development of reversible-deactivation radical polymerization techniques, has enabled the design of a remarkably wide range of well-defined functional block copolymers, which exhibit spontaneous self-assembly either in the bulk or in solution. For example, the formation of diblock copolymer spheres in solvents that are selective for one of the two blocks has been known for more than fifty years. In 1999, Bates and co-workers reported that aqueous dispersions of highly anisotropic poly(ethylene oxide)-polybutadiene worms formed free-standing viscoelastic gels above a certain critical copolymer concentration. Since this seminal study, block copolymer worms have been evaluated for drug delivery, as sterilizable hydrogels for 3D cell culture and stem cell storage,

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Electronic Supplementary Information (ESI) available: Experimental section; Kinetic study; Assigned 1H NMR spectra; GPC data; Additional TEM images; Additional rheological data; IR spectra; Theoretical calculations for hydrogen bonding dimers; Equilibrium configuration of the methyl acetate dimer; SAXS model. See DOI: 10.1039/x0xx00000x
cryopreservation of red blood cells, as superfloculants for micrometer-sized particles, for viscosity modification, of reinforcement of latex films and as model Pickering emulsifiers. This sub-field has been reviewed by Davis and co-workers and more recently by Tian et al. Traditionally, block copolymer self-assembly in solution has been achieved by post-polymerization processing techniques such as a solvent switch or thin film rehydration, which usually only enable the preparation of rather dilute copolymer dispersions. In contrast, polymer-induced self-assembly (PISA) enables the rational synthesis of block copolymer nano-objects at relatively high copolymer concentrations (up to 50% w/w). In particular, reversible addition-fragmentation chain transfer (RAFT) polymerization has enabled the efficient PISA synthesis of a wide range of functional block copolymer spheres, worms or vesicles in aqueous, alcoholic or non-polar media. Typically, the worm morphology occupies rather narrow phase space. However, Rieger and co-workers recently designed a functional RAFT agent in order to place bis-urea ‘stickers’ within the core-forming block; introducing this hydrogen bonding motif enables the worm phase space to be significantly expanded for an aqueous PISA formulation. Alternatively, constructing an appropriate pseudo-phase diagram based on PISA synthesis provides a reliable means of targeting the otherwise elusive worm morphology. This systematic approach has led directly to many more examples of well-defined block copolymer worms being reported. An additional method of controlling nanoparticle morphology during PISA involves the judicious selection of chain-end functionality. It is now recognized that many PISA formulations based on RAFT dispersion polymerization afford thermoresponsive diblock copolymer worms in either aqueous, alcoholic, or non-polar media. In particular, heating a dispersion of poly(lauryl methacrylate)-poly(benzyl methacrylate) worms in n-dodecane induces a worm-to-sphere morphology transition, which can be fully reversible if conducted at sufficiently high copolymer concentration. The present work focuses on diblock copolymer worms that form free-standing gels at sufficiently high copolymer concentration owing to a percolating network arising from multiple inter-worm contacts. Hydrogen bonding is particularly strong in non-polar media, with one well-known example of such a non-covalent interaction being the dimerization of acetic acid in benzene. In principle, the synthesis of diblock copolymer worms via RAFT-mediated PISA allows free-standing gels to be conveniently introduced at the end of every sterically stabilized worm (see Scheme 1). For methacrylates this RAFT CTA can typically be either a dithioester or triithiocarbonate. For the purposes of the present work, a carboxylic acid-functional triithiocarbonate, (+)-2-cyano-4-(2-phenylethenylsulfanylthiocarbonyl)sulfanylpentanoic acid (PETTC), was utilized. Thus, when the copolymer concentration exceeds the critical gelation concentration, this should lead to the formation of carboxylic acid dimers at the point where neighboring worms just touch each other to form the 3D network.
Results and discussion

Synthesis of HOOC-PSMA$_{11}$ and H$_2$COOC-PSMA$_{11}$ homopolymer precursors via RAFT solution polymerization of SMA

A kinetic study of the RAFT solution polymerization of SMA in toluene at 70 °C was conducted by periodically removing aliquots of the reaction mixture for analysis over a 7 h period (see Figure S1). Monomer conversions were calculated using $^1$H NMR spectroscopy by comparing the integrated monomer vinyl proton signals at 5.6 and 6.2 ppm with the two oxymethylene protons assigned to the monomer/polymer at 4.0 ppm. A monotonic increase in monomer conversion with polymerization time was observed (see Figure S1a). There are two distinct regimes: initial relatively slow polymerization for the first 100 min, followed by a faster rate of polymerization that obeys first-order kinetics with respect to SMA, as judged by the linear semi-logarithmic plot. The GPC curves shown in Figure S1b were analyzed using a refractive index detector and poly(methyl methacrylate) calibration standards: a linear evolution in $M_n$ with conversion was observed (see Figure S1c) and a relatively narrow molecular weight distribution was obtained for the final PSMA homopolymer ($M_n = 3.100 \text{ g mol}^{-1}$; $M_w/M_n = 1.18$; 93% conversion). Informed by this kinetic study, SMA was polymerized on a 40-gram scale under the same conditions and quenched after 6 h (76% conversion) to ensure retention of the thioicarbonate-based RAFT chain-ends. After purification via precipitation into excess ethanol, the resulting HOOC-PSMA macro-CTA had a mean degree of polymerization (DP) of 11 as judged by $^1$H NMR spectroscopy, while THF GPC analysis indicated an $M_n$ of 5400 g mol$^{-1}$ and an $M_w/M_n$ of 1.11.† Esterification of this HOOC-PSMA$_{11}$ precursor using excess methanol produced the corresponding H$_2$COOC-PSMA$_{11}$ macro-CTA (see Scheme 1a). $^1$H NMR spectroscopy confirmed successful end-group derivatization: comparison of the integrated terminal methyl ester proton signal at 3.7 ppm to that of the oxymethylene proton signal assigned to the SMA repeat units at 4.0 ppm indicated that the degree of

![Route 1: in situ PISA approach](Image)

![Route 2: post-polymerization processing strategy](Image)

Scheme 2. Schematic representation of the two synthetic routes used herein to prepare the two series of PSMA-PBzMA worms containing varying proportions of carboxylic acid end-groups. Both routes are based on the principle of entropic mixing. Route 1 utilizes a binary mixture of HOOC-PSMA$_{11}$ and H$_2$COOC-PSMA$_{11}$ precursors during the RAFT dispersion polymerization of BzMA; this approach results in a statistical distribution of carboxylic acid end groups located at the outer surface of each sterically-stabilized worm. Route 2 involves heating two ‘masterbatch’ 20% w/w dispersions comprising HOOC-PSMA$_{11}$-PBzMA$_{65}$ and H$_2$COOC-PSMA$_{11}$-PBzMA$_{65}$ worm gels up to 110 °C to induce a worm-to-sphere transition (and concomitant degelation) in each case. These two free-flowing fluids of spherical nanoparticles were then mixed together in various proportions at this temperature to produce the desired range of carboxylic acid/methyl ester molar ratios. On cooling to 20 °C, a sphere-to-worm transition occurs via 1D stochastic fusion of multiple (mixed) spheres to produce ‘hybrid’ segmented worms comprising spatially-localized patches of steric stabilizer chains bearing carboxylic acid end-groups.
Retention time (min)

| Gels                        | Mn (g mol⁻¹) | Mw/Mn |
|-----------------------------|-------------|-------|
| HOOC-PSMA₁₁-PBzMA₃₈        | 10 300      | 1.12  |
| HOOC-PSMA₁₁-PBzMA₆₅        | 13 400      | 1.14  |
| HOOC-PSMA₁₁-PBzMA₉₅        | 15 400      | 1.18  |
| HOOC-PSMA₁₁-PBzMA₁₄₄       | 15 400      | 1.24  |
| HOOC-PSMA₁₁-PBzMA₁₇₄       | 20 400      | 1.24  |
Figure 2. Representative transmission electron micrographs recorded for 0.10% w/w dispersions of the ten examples of PSMA-PBzMA diblock copolymer worms prepared using Route 1 and Route 2 in this study (see Scheme 2). Insets show digital photographs recorded for the corresponding ten worm gels at 10% w/w solids. This so-called tube inversion test confirms their free-standing nature at ambient temperature.
significantly greater inter-worm interactions for the former gel. Interestingly, the worm gels prepared via Route 2 typically exhibit higher $G'$ values than the equivalent worm gels prepared via Route 1. In principle, this suggests that a relatively high local concentration of carboxylic acid end-groups favors the formation of multiple carboxylic acid dimers at the point(s) of contact between neighboring worms. However, in principle the $G'$ values obtained for the two pairs of worm gels containing no carboxylic acid groups ($n = 0$) and solely carboxylic acid groups ($n = 1.00$) should be identical. Thus the observed difference between each pair of measurements shown in Figure 3a most likely indicates the experimental uncertainty in these rheological experiments (estimated to be 30-50%). In this context, it is worth emphasizing that the 25-fold boost in $G'$ is much larger than this experimental uncertainty.

Temperature-dependent oscillatory rheology studies provide further evidence for hydrogen bonding interactions between carboxylic acid-functionalized worms (see Figure S7). The purpose of these experiments was to determine the critical gelation temperature (CGT), which is the temperature above which the dispersion is no longer a gel (i.e. where $G''$ exceeds $G'$). A worm gel containing solely HOOC-PSMA$_{11}$-PBzMA$_{65}$ exhibited a CGT of 92 °C, whereas the CGT of H$_2$COOC-PSMA$_{11}$-PBzMA$_{65}$ worm gel containing no carboxylic acid groups was significantly lower (41 °C). Similarly, a significant difference is observed for the critical gelation concentration (CGC), which is defined as the minimum concentration at which a free-standing gel can be obtained (see Figure 3b and 3c). We have previously shown that reducing the copolymer concentration of worm gels leads to degelation due to the reduction in the number of inter-worm contacts that form the gel network. For HOOC-PSMA$_{11}$-PBzMA$_{65}$ (n = 1.00) and H$_2$COOC-PSMA$_{11}$-PBzMA$_{65}$ (n = 0) dispersions, SAXS patterns were recorded at a copolymer concentration of 1.0% w/w (see Figure 4). In both cases, an approximate $I(q) \sim q^{-2}$ dependence was observed in the low q region, which is consistent with a well-defined worm-like morphology. Moreover, the local minima observed at high q indicate that these two types of worms exhibit the same mean worm core cross-sectional diameter. Indeed, fitting these data to a well-established worm-like micelle model confirmed that the mean overall worm thickness ($T_{worm} = 2R_{wc} + 4R_{g}$, where $R_{wc}$ is the mean worm core radius and $R_{g}$ is the radius of gyration of the stabilizer chains) for these two samples were 16.8 and 16.6 nm, respectively. Furthermore, the mean worm length ($L_{worm}$)
was determined to be approximately 900 nm for both worms exhibit a pronounced upturn in X-ray scattering intensity dispersions. However, the HOOC-PSMA_{11}-PBzMA_{65} (n = 1.00) at low q compared to the H\textsubscript{2}COOC-PSMA_{11}-PBzMA_{65} (n = 0) worms. An /I(q) = Bq\textsuperscript{P} relationship was incorporated into the scattering model to account for this effect, whereby higher P values indicate a steeper slope in the low q region. Indeed, a P value of 1.95 was determined for the HOOC-PSMA_{11}-PBzMA_{65} (n = 1.00) worms, whereas the H\textsubscript{2}COOC-PSMA_{11}-PBzMA_{65} (n = 0) worms have a P value of only 1.63. This suggests significantly stronger inter-worm interactions for the former copolymer dispersion. More specifically, we hypothesize that such interactions involve the formation of hydrogen-bonded carboxylic acid dimers (see Scheme 3).

Recently we reported\textsuperscript{25} that, to a reasonable first approximation, the gelation behavior of block copolymer worms can be rationalized in terms of the percolation theory developed by Chatterjee for polydisperse rods.\textsuperscript{81} This suggests that multiple inter-worm contacts (rather than worm entanglements, which have been invoked to account for the gelation behavior observed for surfactant-based worms\textsuperscript{82-84}) are sufficient to form a 3D gel network. Furthermore, the critical worm volume fraction, \( \varphi_w \), required for macroscopic gelation scales with the mean worm radius, \( R \), and the weight-average worm length, \( L_w \), according to the simple relationship \( \varphi_w \sim R/L_w \).\textsuperscript{75} Fitting the SAXS data shown in Figure 4 to a well-established worm-like micelle model\textsuperscript{78} confirms that the mean dimensions (i.e. \( R \) and \( L_w \)) for worms prepared using the carboxylic acid-based RAFT agent alone (\( n = 1.00 \)) and the methyl ester-based RAFT agent alone (\( n = 0 \)) are almost identical (see above). Thus, percolation theory predicts that these two types of worm gel should exhibit essentially the same behavior.

However, the rheological data shown in Figure 3a and digital images shown in Figure 3b and 3c clearly indicate substantial differences in both the CGC (or \( \varphi_c \)) and the CGT. This is consistent with additional attractive forces operating between neighboring worms, which leads to significantly stronger inter-worm interactions.

**Spectroscopic investigations of hydrogen bonding**

We now present indirect spectroscopic evidence that such non-covalent interactions actually involve carboxylic acid dimer formation (see Scheme 3). Conventional hydrogen bonds such as those formed between water molecules exhibit enthalpies of dissociation of ~23 kJ mol\(^{-1}\) at 298 K.\textsuperscript{86} However, the enthalpy of dissociation for carboxylic acid dimers is significantly stronger, typically ~34 kJ mol\(^{-1}\) for acetic acid dimers in benzene at 298 K.\textsuperscript{86} In principle, the presence of hydrogen-bonded dimers could be confirmed by observing the splitting of the acid carbonyl stretching vibration into an IR-active and a Raman active component or by observing frequency shifts between the carboxylic acid-functionalized worms and the ester-functionalized worms. Unfortunately, obtaining direct spectroscopic evidence for the formation of carboxylic acid dimers between neighboring block copolymer worms in n-dodecane is not experimentally feasible for three reasons. First, there is only one carboxylic acid end-group per block copolymer chain. On the other hand, each chain contains on average 76 methacrylic ester repeat units, which absorb IR radiation at a very similar frequency (approximately 1700 cm\(^{-1}\) for carboxylic acids and 1720-1740 cm\(^{-1}\) for esters). Second, unless the worms are aligned under flow, only a rather small proportion of carboxylic acid end-groups are expected to be involved in the formation of carboxylic acid dimers between neighboring worms when forming a percolating 3D gel network via inter-worms contacts.\textsuperscript{75} Finally, carboxylic acid dimer formation within individual worms is not spectroscopically distinguishable from that between neighboring worms, although only the latter species contributes to stronger worm gels.

Nevertheless, indirect evidence for carboxylic acid dimer formation can be obtained by FT-IR spectroscopy studies of each of the two PSMA\(_{11}\) precursors dissolved in n-dodecane (see Figure S8). In this case, there is one carboxylic acid end-group per eleven methacrylic ester repeat units, which makes it much easier to observe IR signatures arising from the former species. Thus, by working at a relatively high concentration (50% w/w), a wavenumber shift of approximately ~10 cm\(^{-1}\) can be observed in the carbonyl region, which is in semi-quantitative agreement with theoretical calculations that predict a more pronounced red shift for carboxylic acid dimers compared to ester dimers (see details in the Supporting Information). Thus there is reasonable experimental and theoretical evidence to suggest that carboxylic acid-functionalized worms should exhibit much stronger hydrogen bonding interactions compared to ester-functionalized worms. This is expected to boost the bulk modulus observed for the former worm gels, as observed in the rheological studies reported herein.
Conclusions

We report two complementary entropic mixing strategies for boosting the bulk modulus of sterically-stabilized poly(stearyl methacrylate)-poly(benzyl methacrylate) diblock copolymer worm gels via hydrogen bonding interactions. This is achieved simply by introducing carboxylic acid groups at the end of the poly(stearyl methacrylate) stabilizer chains, which leads to the formation of carboxylic acid dimers between neighboring worms in non-polar media. Unlike many other literature examples of hydrogen-bonded polymer systems, introducing this structural motif involves minimal synthetic effort because the RAFT polymerization chemistry employed to prepare these diblock copolymer worms typically utilizes carboxylic acid-based RAFT agents. Thus, using binary mixtures of carboxylic acid- and methyl ester-functionalized poly(stearyl methacrylate) stabilizers for the RAFT dispersion polymerization of benzyl methacrylate (Route 1) enables the storage gel modulus, $G'$, to be systematically varied from ~4.5 kPa up to ~114 kPa. A similar variation in gel strength can be achieved by exploiting the thermoreversible worm-to-sphere transition exhibited by such worm gels. Thus, mixing concentrated dispersions of free-flowing carboxylic acid- and methyl ester-functionalized spheres together at 110 °C leads to the formation of ‘hybrid’ segmented worms on cooling to ambient temperature via stochastic 1D fusion of multiple spheres (Route 2). Moreover, SAXS studies indicate that significantly stronger inter-worm interactions can be achieved when using a carboxylic acid-based RAFT agent for such worm gel syntheses, while rheological studies indicate both a significant reduction in critical gelation concentration (from approximately 10% w/w to 2-3% w/w) and a substantial increase in critical gelation temperature (from 41 °C to 92 °C). In summary, this study highlights how the introduction and judicious modulation of non-covalent interactions can be used to tune the physical properties of block copolymer worm gels, thus providing significant improvements in gel strength, gelation efficiency and gel cohesion.

Author Contributions

M.J.D. and S.P.A conceived the project. E.R. performed all syntheses and obtained NMR, GPC, rheology and FT-IR data. M.J.D. performed TEM and SAXS analyses. M.F.A.H. conducted quantum chemical calculations. All co-authors contributed to the writing, reviewing and editing of this manuscript.

Conflicts of interest

There are no conflicts to declare.

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