

Durham Research Online

Deposited in DRO:

19 February 2013

Version of attached file:

Accepted Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

Hutchings, Lian R. and Kimani, Solomon M. and Hoyle, David M. and Read, Daniel J. and Das, Chinmay and McLeish, Thomas C. B. and Chang, Taihyun and Lee, Hyojoon and Auhl, Dietmar (2012) 'In silico molecular design, synthesis, characterization, and rheology of dendritically branched polymers : closing the design loop.', ACS macro letters., 1 (3). pp. 404-408.

Further information on publisher's website:

<http://dx.doi.org/10.1021/mz300059k>

Publisher's copyright statement:

This document is the Accepted Manuscript version of a Published Work that appeared in final form in ACS macro letters, copyright © American Chemical Society after peer review and technical editing by the publisher. ACS macro letters.

Additional information:

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a [link](#) is made to the metadata record in DRO
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full DRO policy](#) for further details.

In Silico Molecular Design, Synthesis, Characterization, and Rheology of Dendritically Branched Polymers: Closing the Design Loop

Lian R. Hutchings,^{*,†} Solomon M. Kimani,[†] David M. Hoyle,[†] Daniel J. Read,[‡] Chinmay Das,[§] Thomas C. B. McLeish,[†] Taihyun Chang,^{||} Hyojoon Lee,^{||} and Dietmar Auhl^{§,⊥}

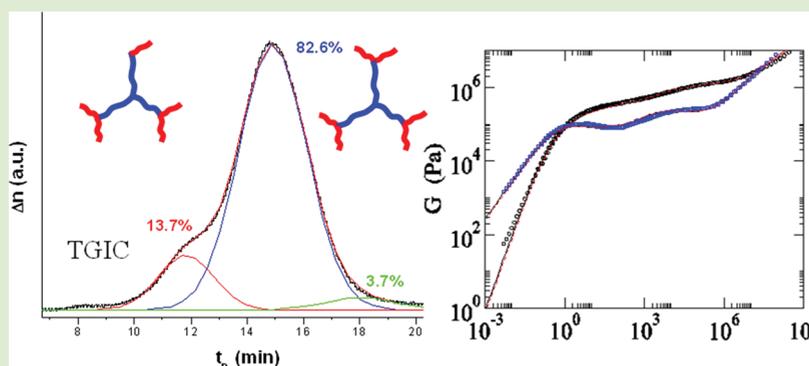
[†]Durham Centre for Soft Matter, Department of Chemistry, Durham University, Durham, DH1 3LE, United Kingdom

[‡]School of Mathematics, University of Leeds, Leeds, LS2 9JT, United Kingdom

[§]School of Physics and Astronomy, University of Leeds, Leeds, LS2 9JT, United Kingdom

^{||}Department of Chemistry and Division of Advanced Materials Science, Pohang University of Science and Technology (POSTECH), Pohang 790784, Republic of Korea

Supporting Information



ABSTRACT: It has been a long held ambition of both industry and academia to understand the relationship between the often complex molecular architecture of polymer chains and their melt flow properties, with the goal of building robust theoretical models to predict their rheology. The established key to this is the use of well-defined, model polymers, homogeneous in chain length and architecture. We describe here for the first time, the in silico design, synthesis, and characterization of an architecturally complex, branched polymer with the optimal rheological properties for such structure–property correlation studies. Moreover, we demonstrate unequivocally the need for accurate characterization using temperature gradient interaction chromatography (TGIC), which reveals the presence of heterogeneities in the molecular structure that are undetectable by size exclusion chromatography (SEC). Experimental rheology exposes the rich pattern of relaxation dynamics associated with branched polymers, but the ultimate test is, of course, did the theoretical (design) model accurately predict the rheological properties of the synthesized model branched polymer? Rarely, if ever before, has such a combination of theory, synthesis, characterization, and analysis resulted in a “yes”, expressed without doubt or qualification.

In recent decades, many studies^{1–14} have been reported into the relationship between the structure of complex, branched polymer architectures and the rich rheology of their melts. The ultimate goal of such studies is to be able to design, theoretically, a polymer melt with specific rheological properties, to synthesize such a melt, and finally to verify that the melt possesses both the target architecture and required properties. We present here such a program of design, synthesis, and characterization for a melt of dendritically branched polymers.

Well-defined, model dendritically branched polymers,^{11,15,16} also known as DendriMacs^{17–19} and Cayley trees,^{4,13,20} are the simplest hierarchically branched (branch-on-branch) architecture with symmetry about a central branch point. For this reason, they are an optimal structure for rheological studies. However, the synthetic methodologies that have been developed to produce such polymers are without exception

complex, multistep procedures, and a direct result of such complex synthetic strategies is the almost unavoidable formation of imperfections and structural heterogeneity as a result of imperfect linking reactions and premature termination of living polymerizations, a point long recognized by synthetic polymer chemists.^{11,16,21,22} It has often been assumed (until recently) that purification by fractionation of the inherently structurally polydisperse products of such syntheses is sufficient to remove imperfections: false assumptions often reinforced by a monomodal, narrow molecular weight distribution obtained by size exclusion chromatography (SEC).

Received: February 3, 2012

Accepted: February 24, 2012

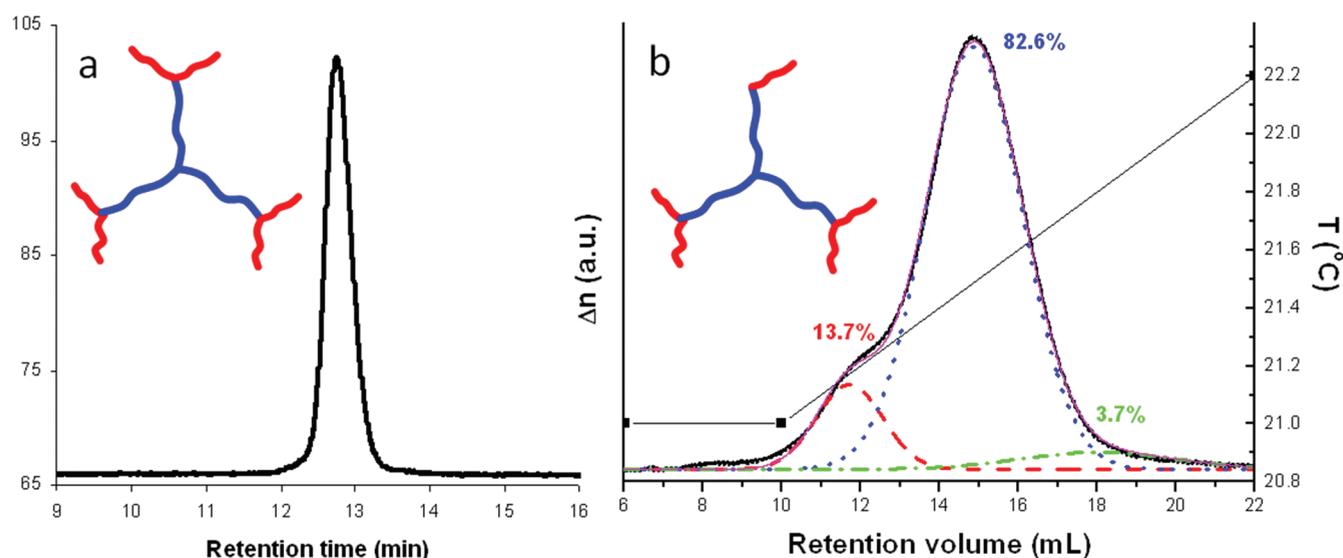


Figure 1. Chromatograms of polybutadiene G1 DendriMac obtained by size exclusion chromatography (a) and temperature gradient interaction chromatography (b). The dotted lines are an estimate of the relative concentrations of each species obtained by deconvolution of the full chromatogram using a gaussian model distribution function.

In parallel to the prodigious efforts of the synthetic polymer chemist, there have been extensive investigations into the development of theoretical models to predict the rheology of complex branched architectures. Such theories form the foundation for computational modeling⁸ and simulation of polymer melt processing and ultimately allow for the design of industrial polymers with specific and desirable properties.²³ Although computational modeling has been used directly for industrially relevant branched polymers, in such melts the polydispersity in molar mass and topology removes specific, identifiable, rheological features from the different levels of branching. Consequently, the use of model polymers has become the standard means for verification of molecular-based rheological models.^{7,11,14,16,24–27} This requires the synthesis of perfectly homogeneous branched polymers or the next best thing, a perfectly characterized *imperfect* polymer, in order to obtain comparative experimental linear rheology. If any uncertainty exists about the veracity of the structure of the synthesized branched polymer, then even minor inconsistencies between experimental rheology and predictions of that rheology leads one to ask the uncomfortable question: is there a problem with the polymer or the theory?

We present here a brief description of the considerations for the *in silico* design, the synthesis and characterization of a 2-level G1 polybutadiene (PB) Cayley tree/DendriMac (see inset of Figure 1a). Moreover, we present temperature gradient interaction chromatography (TGIC) and SEC data to demonstrate the sensitivity of the former and the insensitivity of the latter to small quantities of structural heterogeneity, and finally, we compare the experimental rheology and the theoretical prediction of that rheology, taking into account the presence of imperfections in the branched polymer.

In computational rheology,^{5,8} one considers an ensemble of polymers and follows their interconnected relaxation after a small step strain. The program suite BoB²⁸ allows for the creation of a number of different polymer types and prediction of the rheological properties of such polymers. A two-level DendriMac is the simplest branched polymer in which relaxation occurs purely by retraction of a “compound” arm.

To produce an optimal DendriMac for rheological study, the design criteria we used were the following: there should be well-separated signatures for the relaxation of the two levels and the entire relaxation spectra should be within the experimental range of rheological measurement. In the present study we chose PB (with a high 1,4-microstructure) because of its low glass transition temperature ($T_g \sim 180$ K) and thermal stability under a nitrogen atmosphere even at relatively high temperatures, which allows for an effective frequency window of 12 decades in rheological measurements. For the inner and outer segments to have a similar width of relaxation spectrum (i.e., the ratio of fastest to slowest relaxation time within a given segment), we designed a DendriMac in which the inner segments were twice the molecular weight of the outer segments. Using literature values of τ_e and M_w , the molar masses of the segments were chosen such that the outer segment relaxes at $\sim 3.5 \times 10^3 \tau_e$ and the inner segments at $\sim 7 \times 10^7 \tau_e$. Following a few trials using the BoB software, the outer segments were chosen to be 7500 g/mol (and the inner segments to be 15000 g/mol). The predictions of the rheology modeling satisfied the criteria of the two relaxation times with pronounced peaks in the dissipative modulus within the experimentally realizable frequency window.

The synthesis of the 2-level PB DendriMac was achieved, as previously described,¹⁷ by combining living anionic polymerization and well-established chlorosilane star coupling chemistry^{29,30} with the more recently established macromonomer strategy.¹⁹ Briefly, the first step involved the synthesis of an asymmetric three-arm star with two short arms (M_w 7600 g mol⁻¹) and one long arm (M_w 15300 g mol⁻¹). The long arm, which would become the inner segment of the DendriMac, was end-functionalized at its free end with a protected primary alcohol group, introduced by the use of 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium as the polymerization initiator. The resulting asymmetric star polymer was purified by fractionation using toluene/methanol as the solvent/nonsolvent system before the primary alcohol functionality was deprotected via a mild acid hydrolysis and converted to an alkyl bromide functionality using $\text{CBr}_4/\text{PPh}_3$ to yield an asymmetric 3-arm

star containing a single peripheral alkyl bromide functionality. A Williamson coupling reaction between the alkyl bromide moiety on the mikto arm star and a multifunctional core (1,1,1-tris(4-hydroxyphenyl)ethane) in the presence of cesium carbonate at 55 °C yielded the G1 DendriMac after 24 h. Fractionation of the crude DendriMac to remove undesirable side products resulted in an apparently well-defined branched structure with a narrow polydispersity ($M_w/M_n = 1.05$), as evidenced by a monomodal SEC trace (see Figure 1). The molecular weights of each of the arms of the mikto star, the three-arm mikto star and the G1 DendriMac, were obtained by triple detection SEC, in THF at 30 °C, and are shown in Table 1; all are in excellent agreement with predicted molecular

Table 1. Molecular Weight Data for Polybutadiene G1 DendriMac Obtained by SEC and TGIC and Weight Average Molecular Weight of Imperfect G1 DendriMac Estimated by TGIC

sample	SEC data; molar mass/g mol ⁻¹			PDI
	predicted M_n	expt M_n	expt M_w	
short arm	7500	7000	7250	1.04
long arm	15000	14700	15200	1.03
3-arm star	28700	28600	30500	1.06
G1 DendriMac	85800	85700	90100	1.05
G1 DendriMac ^a	85800		87000	
G1 Defect ^a	78700		79000	

^aMolecular weight estimated from TGIC chromatogram using online triple detection with light scattering.

weights. Further details of SEC analysis can be found as Supporting Information.

Size exclusion chromatography (SEC) has long been the primary method for the characterization of polymer molecular weight and molecular weight distribution. However, due to its mode of separation (by molecular size rather than molecular weight), SEC has an intrinsic limitation, namely, that it is incapable of separating polymers with identical or nearly identical hydrodynamic volumes, which may differ in other molecular parameters such as molecular weight or chain architecture. Such a limitation is a particular concern for the characterization of model branched polymers for structure–property correlation studies. Even with the most sophisticated synthetic strategy, utilizing living anionic polymerization, it is often impossible to synthesize branched polymers with a perfectly uniform chain structure, and small amounts of imperfect byproduct are formed as a result of incomplete branching. Although SEC results may suggest a high degree of molecular homogeneity, the detection of significant levels of branched byproduct is often impossible given the very small differences in hydrodynamic volume. The presence of even small quantities of defects and byproduct can have significant implications when relating the polymer structure to experimental rheology, whereby discrepancies make the validation and subsequent modification of theoretical models impossible. TGIC, a technique that was first described 15 years ago,³¹ has been shown to offer a solution to the limitations displayed by SEC. TGIC separation is driven by enthalpic interactions between the solute molecules and the stationary phase, and these interactions, which can be controlled by temperature variation during the elution, are to a first approximation proportional to the molecular weight NOT the hydrodynamic volume.^{32,33} In the past few years, TGIC has emerged as a

particularly valuable tool for the analysis of complex model-branched polymers. TGIC has recently been exploited to analyze the distribution of number or arms in polystyrene comb branched polymers,^{27,34} to detect structural polydispersity in H-shaped polybutadiene,^{26,35} and to analyze the impact of structural imperfections upon the rheology of H-shaped polybutadiene and H-shaped polybutadiene with an additional branch on the backbone.²⁷ In all of these cases, TGIC revealed that the synthetic strategy, based on living anionic polymerization and chlorosilane coupling, resulted in a myriad of potential structures and, therefore, structural polydispersity. Although purification was possible in some cases, in other cases, structural imperfections with molecular weights and molecular sizes nearly identical to that of the target molecule could not be removed by fractionation.^{27,22} In the present study, SEC analysis of the 2-level DendriMac (following fractionation) indicated a monomodal peak with a narrow polydispersity (1.05) see Table 1 and Figure 1a. However, TGIC analysis revealed the presence of a lower molecular weight species (at lower retention volumes) as evidenced by a shoulder on the TGIC chromatogram, Figure 1b. Details of the SEC and TGIC experimental procedures can be found in Supporting Information. Online molecular weight analysis allowed an estimation of the molecular weight of the main peak and shoulder on the TGIC chromatogram and the data is included in Table 1. The molecular weights obtained for the DendriMac from SEC and TGIC are in good agreement and the estimated M_w of the shoulder is 79000 g mol⁻¹. It would seem most likely that the structure of the lower molecular weight byproduct is that inset in Figure 1b, that is, a G1 DendriMac with one of the outer arms missing. The M_w (by SEC) of the DendriMac is 90100 g mol⁻¹ and the M_w of the outer arm is 7250 g mol⁻¹; therefore, we would expect the M_w of such an imperfection to be approximately 83000 g mol⁻¹. Although this value is a little higher than that estimated (by TGIC) of the defect structure, errors arising from the fact that the shoulder is not well-resolved from the main peak may account for this discrepancy. Regardless of this slight discrepancy, we still believe that the illustrated structure is most likely. However, to explain how such an imperfect structure could arise, we must revisit the synthetic scheme (see Scheme 1 of Supporting Information). One obvious possible explanation is incomplete linking of the outer arm in the synthesis of the intermediate asymmetric 3-arm star. Unfortunately, TGIC analysis of the intermediate star was not carried out so we cannot verify that possibility. However, a second possible explanation lies in the susceptibility of the branch point linkage to cleavage under the conditions (mild acid hydrolysis) used to deprotect the primary alcohol functionality. Quirk et al.³⁶ have previously reported arm cleavage when hydrolysis was carried out for a prolonged reaction time in an identical deprotection reaction on similar star branched polymers: an observation that we also initially made during the synthesis of the DendriMac.¹⁷ To minimize arm cleavage, the deprotection reaction was carried out under high vacuum for only 30 min in presence of BHT (0.1% w/w) at 70 °C, however, it is possible that arm cleavage was not completely eliminated. Although the intermediate star was fractionated to give a monomodal, narrow polydispersity peak, it is likely that SEC would be unable to resolve the star from traces of the defect with one of the shorter arms missing, and such a defect would be able to take part in the subsequent coupling reactions to form the DendriMac. However, it is possible that the increase in PDI in linking the arms to form the

star is indicative of the presence of the defect structure. It is disappointing for the chemist to discover such impurities in their product; however, it is worth noting that, although the imperfect structure is present at a total weight percent of 14%, this in fact means that only 5% of the compound arms have a missing outer arm or (equivalently) that only 2.5% of the outer arms are missing. We believe that these results demonstrate an unprecedented level of both structural characterization and structural homogeneity for a Cayley tree type polymer. It is also worth noting that the TGIC data (Figure 1b) shows some evidence of slight broadening to higher retention volumes, possibly suggesting the presence of a trace of a high molecular weight defect structure. Deconvolution of the TGIC data suggests if such a defect is present, it is present at a very low concentration. One possible source of this high molecular weight defect is the formation of small amount of the intermediate asymmetric star polymer with two long arms and one short arm which could in turn result in a DendriMac in which one of the compound arms has one long outer arm and one short outer arm. It is conceivable that such a defect could arise as a result of the synthetic methodology shown in Scheme 1 (Supporting Information), although given the very low concentration, we cannot be absolutely certain of its presence.

Rheological measurements were carried out using a strain-controlled rheometer (ARES, Rheometric Scientific) with cone and plate geometry under a nitrogen environment at small amplitude oscillatory shear. Results from different temperatures (188–323 K) were used to determine the master curve at 298 K by using time–temperature superposition. Figure 2 shows

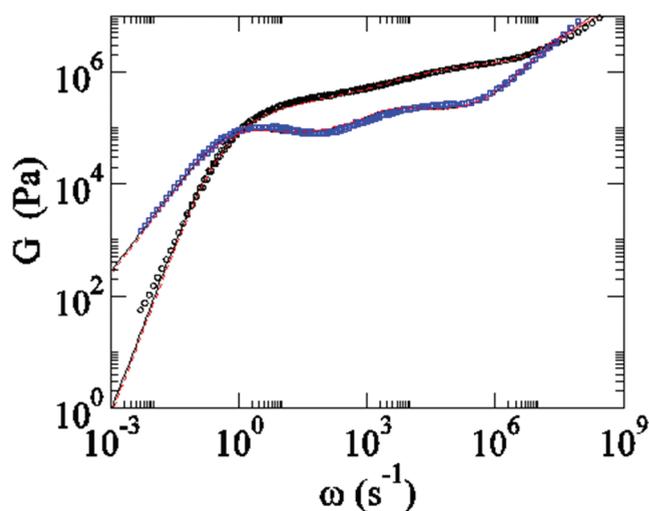


Figure 2. Rheological moduli of G1 DendriMac from small amplitude shear experiments (symbols) and the computational prediction of the same, with segment lengths chosen from the SEC measurements (lines). The dashed red line considers perfect DendriMacs, while the solid black line considers 14% by mass of the material having one of the outer segments missing (as suggested from the TGIC measurements).

the prediction from numerical computation (lines) superposed with the experimental master curve (symbols). For the computation, an ensemble of perfect DendriMacs was created with molar mass and polydispersity selected from the SEC results (dashed lines). We also considered the effect of the presence of defect structures in the DendriMac (solid lines), as suggested by the TGIC results (14% by mass of the in silico

molecules were considered with one of the outer segments missing). The overwhelming impression of the data in Figure 2 is that the experimental data agrees tremendously well with predicted data, which accurately captures the relevant features of the rheology. The only discrepancy between predicted and experimental data is found at very low frequencies. The other striking feature of this data is that the two predictions are themselves extremely similar, suggesting that the presence of a very low concentration of missing outer arms makes little difference to the linear rheology in this case. Other studies, considering the distribution of a number of arms in a comb polymer²⁵ or the presence of defects in the synthesis of H-polymers or regular combs²⁷ have also noted that impurities have only a small effect on linear rheology or, in some cases, where multiple defect structures exist; they can effectively cancel each other out.²⁷ That of course does not in any way negate the value of the TGIC data or the technique or the chemists' attempts to produce perfect structures. Satisfied that the computational model faithfully describes the experimental data, we studied a number of hypothetical ensembles of molecules with different segmental and architectural polydispersities to further establish the impact of varying concentrations of the defect structure upon the predicted rheology (see Figure S1, Supporting Information). It is clear from these data that only significant concentrations (>25%) of the described defect have a significant impact on the linear rheology. We would expect the impact of the possible presence of the higher molecular defect structure on both experimental rheology and the predictions to be immeasurable given the very low concentration and the likely similarity of the structure to the pure DendriMac. To confirm this expectation we have carried out a computational prediction of the rheology of a mixture of products comprised of 82% perfect DendriMac, 14% low molecular weight defect (one outer arm missing), and 4% high molecular weight defect (one long outer arm and one shorter outer arm). This data is presented as Figure S2 in Supporting Information. As expected, rheology is insensitive to the presence of this possible high molecular weight defect, if it is there.

We have described here the in silico design, synthesis, characterization, and rheology (experimental and predicted) of a two-level polybutadiene DendriMac. Despite extremely careful synthesis and purification, we have demonstrated the presence of low concentrations of defect structures, and we have unequivocally shown the sensitivity and value of using TGIC alongside the more commonly used SEC for structural and molecular weight analysis. Moreover, we believe that these results demonstrate an unprecedented level of both structural characterization and structural homogeneity for a Cayley tree type polymer. It is clear that even a polydispersity index (obtained by SEC) as low as 1.05 can mask the presence of imperfections. Moreover, we have shown that rheological response is a sensitive test for the branching topology for entangled polymer melt. The agreement between the experimental rheology for the two-level DendriMac and the predicted rheology of the same is extraordinarily good; however, we have shown, in this letter, that sensitivity to structural defects in this case is finite. The presence of low concentrations of the described defect structure (exposed by TGIC) has little impact on the predicted (and one would assume the experimental) rheology of a two-level DendriMac.

■ ASSOCIATED CONTENT

● Supporting Information

Details of the SEC and TGIC experimental procedures, a full reaction scheme for the synthesis of the two-level DendriMac, and a range of computational predictions of the rheology of DendriMacs contaminated with varying amounts of the described imperfections. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: l.r.hutchings@durham.ac.uk

Present Address

¹Bio and Soft Matter, Université Catholique de Louvain, Croix du Sud 1, Belgique.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of the Engineering and Physical Sciences Research Council for financial support across a number of years. Much of the work described here was carried out as part of the MuPP project (GR/T11838/01). T.C. acknowledges the supports from NRF via NRL (R0A-2007-000-20125-0), SRC (R11-2008-052-03002), and WCU (R31-2008-000-10059-0) programs

■ REFERENCES

- (1) McLeish, T. C. B. *Europhys. Lett.* **1988**, *6*, 511.
- (2) McLeish, T. C. B.; Larson, R. G. *J. Rheol.* **1998**, *42*, 81.
- (3) McLeish, T. C. B.; Allgaier, J.; Bick, D. K.; Bishko, G.; Biswas, P.; Blackwell, R.; Blottiere, B.; Clarke, N.; Gibbs, B.; Groves, D. J.; Hakiki, A.; Heenan, R. K.; Johnson, J. M.; Kant, R.; Read, D. J.; Young, R. N. *Macromolecules* **1999**, *32*, 6734.
- (4) Blackwell, R. J.; Harlen, O. G.; McLeish, T. C. B. *Macromolecules* **2001**, *34*, 2579.
- (5) Larson, R. G. *Macromolecules* **2001**, *34*, 4556.
- (6) McLeish, T. C. B. *Adv. Phys.* **2002**, *51*, 1379.
- (7) Kapnistos, M.; Vlassopoulos, D.; Roovers, J.; Leal, L. G. *Macromolecules* **2005**, *38*, 7852.
- (8) Das, C.; Inkson, N. J.; Read, D. J.; Kelmanson, M. A.; McLeish, T. C. B. *J. Rheol.* **2006**, *50*, 207.
- (9) Inkson, N. J.; Graham, R. S.; McLeish, T. C. B.; Groves, D. J.; Fernyhough, C. M. *Macromolecules* **2006**, *39*, 4217.
- (10) Nielsen, J. K.; Rasmussen, H. K.; Denberg, M.; Almdal, K.; Hassager, O. *Macromolecules* **2006**, *39*, 8844.
- (11) van Ruymbeke, E.; Orfanou, K.; Kapnistos, M.; Iatrou, H.; Pitsikalis, M.; Hadjichristidis, N.; Lohse, D. J.; Vlassopoulos, D. *Macromolecules* **2007**, *40*, 5941.
- (12) Zhou, Q.; Larson, R. G. *Macromolecules* **2007**, *40*, 3443.
- (13) Watanabe, H.; Matsumiya, Y.; van Ruymbeke, E.; Vlassopoulos, D.; Hadjichristidis, N. *Macromolecules* **2008**, *41*, 6110.
- (14) Ahmadi, M.; Bailly, C.; Keunings, R.; Nekoomanesh, M.; Arabi, H.; van Ruymbeke, E. *Macromolecules* **2011**, *44*, 647.
- (15) Orfanou, K.; Iatrou, H.; Lohse, D. J.; Hadjichristidis, N. *Macromolecules* **2006**, *39*, 4361.
- (16) Lee, J. H.; Orfanou, K.; Driva, P.; Iatrou, H.; Hadjichristidis, N.; Lohse, D. J. *Macromolecules* **2008**, *41*, 9165.
- (17) Kimani, S. M.; Hutchings, L. R. *Macromol. Rapid Commun.* **2008**, *29*, 633.
- (18) Hutchings, L. R.; Roberts-Bleming, S. J. *Macromolecules* **2006**, *39*, 2144.
- (19) Hutchings, L. R. *Soft Matter* **2008**, *4*, 2150.
- (20) van Ruymbeke, E.; Muliawan, E. B.; Hatzikiriakos, S. G.; Watanabe, T.; Hirao, A.; Vlassopoulos, D. *J. Rheol.* **2010**, *54*, 643.
- (21) Park, S.; Cho, D.; Im, K.; Chang, T.; Uhrig, D.; Mays, J. W. *Macromolecules* **2003**, *36*, 5834.
- (22) Perny, S.; Allgaier, J.; Cho, D. Y.; Lee, W.; Chang, T. Y. *Macromolecules* **2001**, *34*, 5408.
- (23) Read, D. J.; Auhl, D.; Das, C.; den Doelder, J.; Kapnistos, M.; Vittorias, I.; McLeish, T. C. B. *Science* **2011**, *333*, 1871.
- (24) Clarke, N.; Colley, F. R.; Collins, S. A.; Hutchings, L. R.; Thompson, R. L. *Macromolecules* **2006**, *39*, 1290.
- (25) Chambon, P.; Fernyhough, C. M.; Im, K.; Chang, T.; Das, C.; Embery, J.; McLeish, T. C. B.; Read, D. J. *Macromolecules* **2008**, *41*, 5869.
- (26) Chen, X.; Rahman, M. S.; Lee, H.; Mays, J.; Chang, T.; Larson, R. *Macromolecules* **2011**, *44*, 7799.
- (27) Snijkers, F.; van Ruymbeke, E.; Kim, P.; Lee, H.; Nikopoulou, A.; Chang, T.; Hadjichristidis, N.; Pathak, J.; Vlassopoulos, D. *Macromolecules* **2011**, *44*, 8631.
- (28) <http://sourceforge.net/projects/bob-rheology>.
- (29) Adams, C. H.; Hutchings, L. R.; Klein, P. G.; McLeish, T. C. B.; Richards, R. W. *Macromolecules* **1996**, *29*, 5717.
- (30) Hutchings, L. R.; Richards, R. W. *Polym. Bull.* **1998**, *41*, 283.
- (31) Lee, H. C.; Chang, T. Y. *Polymer* **1996**, *37*, 5747.
- (32) Chang, T. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 1591.
- (33) Ryu, J.; Chang, T. Y. *Anal. Chem.* **2005**, *77*, 6347.
- (34) Ahn, S.; Im, K.; Chang, T.; Chambon, P.; Fernyhough, C. M. *Anal. Chem.* **2011**, *83*, 4237.
- (35) Li, S. W.; Park, H. E.; Dealy, J. M.; Maric, M.; Lee, H.; Im, K.; Choi, H.; Chang, T.; Rahman, M. S.; Mays, J. *Macromolecules* **2011**, *44*, 208.
- (36) Hwang, J.; Foster, M. D.; Quirk, R. P. *Polymer* **2004**, *45*, 873.