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Synthesis and characterization of star-like microgels by one-pot free radical polymerization

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Abstract

A one-pot free radical polymerization process was used to prepare methyl acrylate/ethylene glycol dimethacrylate (MA/EGDMA) and methyl methacrylate/ethylene glycol dimethacrylate (MMA/EGDMA) polymers. The role of monomer and crosslinker reactivity ratios in producing different network structures was demonstrated. While both systems produced branched polymers that exhibited low intrinsic viscosities with little variation across a wide range of molecular weights, the star-like microgels formed between a less reactive monomer (MA) with a more reactive crosslinker (EGDMA) gave lower bulk solution viscosities than the more statistical polymers formed between similarly reactive monomers and crosslinkers (MMA and EGDMA). This paper presented a simple and cost-effective synthetic route for the production of polymers with high molecular weight and low viscosity with considerable potential for industrial-scale processing.

Keywords: Free radical polymerization; Reactivity ratio; Star microgel

1. Introduction

Star-shaped polymers are known to exhibit properties such as good solubility in common organic solvents and much lower solution viscosities compared to linear polymers of comparable molecular weights [1–3]. These unique properties have made them useful in applications ranging from drug delivery [4], membrane formation [5], or as additives in adhesives, paints and coatings [6].

Specialized star-shaped structures with cross-linked microgel cores have been synthesized by a number of polymerization techniques, including cationic [7–9], anionic [10–13], nitroxide-mediated radical (NMRP) [13,14], atom transfer radical (ATRP) [15–28], and reversible addition fragmentation chain transfer radical (RAFT) [29, 30] polymerization. Although these 'controlled' polymerization techniques yield well-defined star structures with narrow polydispersities, problems such as limited choice of monomers and solvents and requirements for stringent reaction conditions (cationic and anionic polymerization), long reaction times to achieve high monomer conversions (ATRP), high costs (ATRP, NMRP), the need to remove metal catalysts (ATRP) and thermal instability of the final products (NMRP, RAFT), have restricted their production on a large scale.

As conventional free radical polymerization presents none of the problems associated with the 'controlled' polymerization methodologies and the reactions can be carried out in a single step, using a wide range of monomers and under a wide range of conditions, the ability to form star-like structures using the conventional scheme has potential for economically viable industrial scale production of these materials.

In this work, we describe the synthesis of star-like polymers by conventional free radical polymerization by exploiting differences in monomer and crosslinker reactivity ratios [17(b)]. Data on monomer and crosslinker conversion from gas chromatography-mass spectrometry (GC–MS), molecular weight and intrinsic viscosity from gel permeation chromatography (GPC), and bulk solution viscosity from cone-and-plate rheometry, will also be presented and discussed.

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2. Experimental section

2.1. Materials

Monomers methyl acrylate (MA, 99%+), methyl methacrylate (MMA, 99%+) and ethylene glycol dimethacrylate (EGDMA, 98%+) (Aldrich), the chemical structures of which are shown in Fig. 1, were purified by passing through a column of basic alumina (Aldrich), inhibitor-remover packing (Aldrich) and stored below 4 °C prior to use. The initiator 2,2-azobis(2-methylpropionitrile) (AIBN) (DuPont Australia Vazo® 64) was recrystallized from ethanol and also stored below 4 °C prior to use. Solvents *p*-xylene (99%+, anhydrous) (Aldrich), methanol (AR grade) (Ajax), tetrahydrofuran (HPLC grade) (Ajax) and 1,4-dioxane (AR grade) (LabScan Analytical Sciences) were used without further purification.

2.2. Methods

2.2.1. Synthesis of polymers MA/EGDMA or MMA/EGDMA

Appropriate amounts of reagents MA (or MMA), EGDMA, AIBN and *p*-xylene were added to a Schlenk tube with mixing and then subjected to three freeze-pump-thaw cycles on the vacuum line (10 Pa) to remove molecular oxygen which is an inhibitor in free radical polymerizations. The total solution volume in each experiment was 8 mL and the exact amount of each component used varied according to the %*T* and %*C* formulation required (%*T* = total mass of monomers (g)/volume of solution (mL) × 100; %*C* = mass of crosslinker (g)/total mass of monomers (g) × 100). The initiator-to-monomer ratio was fixed at 1:100 on a molar basis in each case. The reaction tubes were purged with argon after degassing to avoid creation of a vacuum inside the tubes. The samples were then heated in an oil bath set at 100 °C for up to 72 min (≈10 half-lives of AIBN) [31] or 90 h, depending on the experiments.

2.2.2. Product isolation

After polymerization, the reaction products were isolated. Typically the resulting solution is added dropwise to a large excess of non-solvent to precipitate out any polymers formed. However, we are interested not only in analyzing the polymers formed but also in quantifying the amount of monomers that is left unreacted. A large volume of non-solvent will dilute the residual monomers to below their detection limit. Thus, a minimal and precise amount of chilled methanol was added to the polymer solution and stirred vigorously for a period of time, and then subjected to centrifugation in an Eppendorf 5702 centrifuge at 4400 rpm for 20 min. The addition of chilled methanol serves to stop the polymerization reactions by cold quenching, as well as to simultaneously extract unreacted monomers and precipitate the polymers formed since methanol is a solvent for the monomers but non-solvent for the polymers. The supernatants and precipitates were subsequently collected into separate sample containers for further analyses.

2.2.3. Monomer conversion determination from GC–MS

GC–MS analyses were performed on a Shimadzu GC-17A gas chromatograph equipped with a Zebron ZB-5 capillary column from Phenomenex (solid phase 5%-phenyl-95%-dimethylpolysiloxane; dimensions 30 m × 0.25 mm × 0.25 μm) and coupled to a Shimadzu GCMS-QP5000 electron ionization mass spectrometer. A set of standard curves was first established by measuring the peak areas of each monomer at known concentrations. Good linearity ($r^2 \geq 0.995$) was obtained in each case over the concentration range tested (0.02–2.0 mg/mL). The supernatants were then diluted appropriately and passed through 0.25 mm syringe filters (nylon, pore size 0.45 μm) (Alltech) and then also injected into the GC–MS for analyses. The concentration of unreacted monomers was calculated from the standard curves and the percentage conversion of each monomer ((initial conc. − final conc.)/initial conc. × 100) was also determined. GC conditions for the experiments above were as follows: Carrier gas helium; injection volume 1 μL; injector and detector temperatures 240 and 320 °C, respectively. Temperature gradient was: initial temperature 40 °C; initial time 2 min; rate 10 °C/min; final temperature 230 °C; final time 5 min.

2.2.4. Molecular weight and intrinsic viscosity determination by GPC

The polymer precipitates were dried by solvent evaporation under vacuum (10–50 Pa) and then weighed. These were then made up to the desired concentration of 20 mg/mL by redissolving the dried polymer in appropriate amounts of tetrahydrofuran (THF). The GPC used was a triple detection system with a Wyatt Dawn F laser photometer operating at 90° (right angle laser light scattering, RALLS) coupled with an on-line Waters 410 differential refractometer (for measurement of refractive index, RI) and Viscotek T50A differential viscometer (for measurement of differential pressure, DP) in parallel. The columns used were three Phenogel columns in series from Phenomenex (solid phase sulfonated divinylbenzene; dimensions 30 cm × 7.8 mm × 5 μm, porosities 500, 104 and 106 Å, respectively). Data acquisition and analyses were performed with the Viscotek TriSEC® software. All

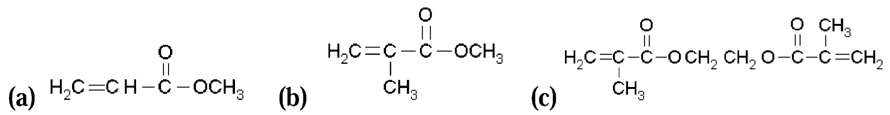

Fig. 1. Chemical structures of (a) methyl acrylate, MA; (b) methyl methacrylate, MMA; and (c) ethylene glycol dimethacrylate, EGDMA.

three detectors were calibrated with poly(methyl methacrylate) (PMMA) standards of known molecular weight and intrinsic viscosity and narrow polydispersity. GPC running conditions were as follows: mobile phase THF; flowrate 1.0 mL/min; injection volume 20 μL; column temperature 30 °C.

2.2.5. *Bulk viscosity measurements from cone-and-plate rheometry*

The polymers were again dried by solvent evaporation under vacuum and weighed, but this time made up to concentrations up to 70% w/w in 1,4-dioxane. The bulk viscosities of the samples were then measured at 25 °C using a Carrimed CSL100 rheometer with cone-and-plate geometry in flow package. Cone dimensions were as follows: diameter 2 cm; angle 0°30′; truncation gap 13 μm. Flow curves were obtained under both controlled shear stress and controlled shear rate modes and the viscosity was determined from the gradient of the shear stress versus shear rate curves.

2.2.6. *Synthesis of star microgel by ATRP method*

Star microgels consisting of EGDMA cores and PMMA arms were synthesized by the two-step arm-first ATRP approach according to our procedure described elsewhere [16]. Data for these microgels were as follows: (1) arm $M_w = 10{,}980$ Da, polydispersity (PD) = 1.1; star microgel $M_w = 505{,}300$ Da, PD = 1.1; number of arms = 31; (2) arm $M_w = 37{,}250$ Da, PD = 1.1; star microgel $M_w = 362{,}000$ Da, PD = 1.1; number of arms = 9; (3) arm $M_w = 47{,}830$ Da, PD = 1.1; star microgel $M_w = 588{,}000$ Da, PD = 1.1; number of arms = 11; (4) arm $M_w = 55{,}860$ Da, PD = 1.1; star microgel $M_w = 731{,}900$ Da, PD = 1.2; number of arms = 12.

3. Results and discussion

Initially, the %*T* and %*C* compositions for the syntheses of soluble high molecular weight polymers without macrogel formation were established using both MA/EGDMA and MMA/EGDMA systems. The kinetic process of both systems was then followed to monitor the conversion of each monomer. The polymers were also characterized to obtain their physical and rheological properties.

3.1. *Polymer domains*

The %*T* and %*C* formulation was varied for both MA/EGDMA and MMA/EGDMA systems and different domains were obtained, as shown in Fig. 2(a) and (b). The polymerization time was fixed at 90 h in these experiments.

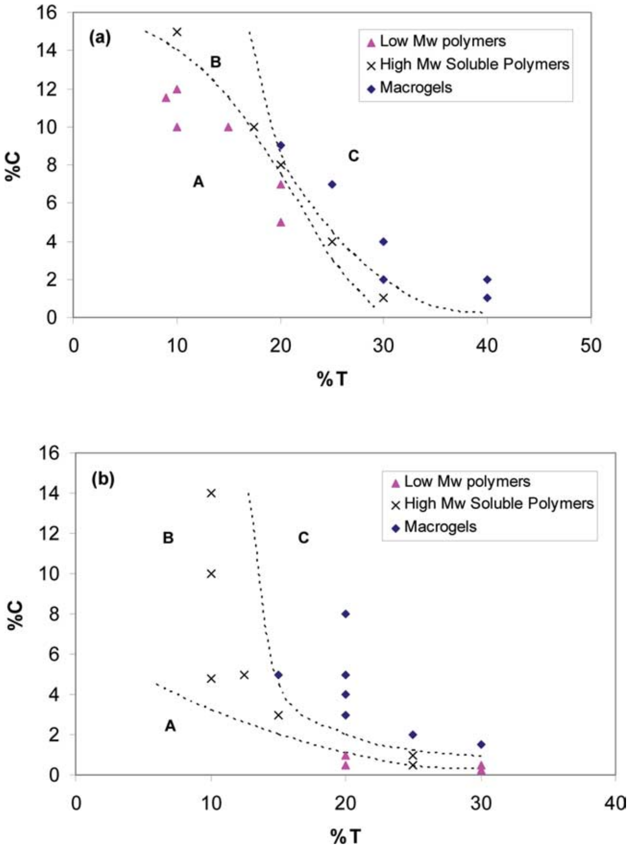

Fig. 2. Different domains for (a) MA/EGDMA and (b) MMA/EGDMA polymers, synthesized by free radical polymerization in *p*-xylene at 100 °C for 90 h, using AIBN (Vazo® 64) as initiator.

It was shown that for both polymer systems, a region existed in which either too high total monomer concentration (%*T*) and/or too much crosslinker (%*C*) resulted in the formation of an intractable, fully crosslinked network (insoluble macrogel; region C). At the other extreme, too low %*T* and/or %*C* resulted in the formation of low molecular weight oligomers, which were difficult to precipitate out of solution (region A). At intermediate %*T* and %*C*, polymers were formed which remained soluble in the polymerization solvent but were also easy to precipitate with addition of methanol (region B). In this region, a higher %*T* in the formulation necessitated the use of a lower %*C* to avoid bulk gel formation.

It was also observed that the MA/EGDMA system allowed higher %*T* and %*C* to be used for the formation of polymers in region B. For example, at a fixed 20%*T*, region B could be produced at 8–9%*C* for MA/EGDMA, but only about 1.5–3%*C* for MMA/EGDMA. Similarly, at a fixed 5%*C*, region B could be produced at around 23%*T* for MA/EGDMA, compared to less than 16%*C* for MMA/EGDMA. Therefore, MA/EGDMA soluble polymers could generally be prepared at higher concentrations than that for MMA/EGDMA. Previously soluble high molecular weight polymers using conventional free radical polymerization could only be formed in very dilute solutions, via intra- or inter-molecular crosslinking between pendant double bonds of vinyl/divinyl monomers as was first demonstrated by Staudinger and Husemann [32].

It was region B that was further studied by GC–MS, GPC and cone-and-plate rheometry in this work.

3.2. Monomer conversion

The conversion of monomers was measured for different %*T* and %*C* formulations at a fixed reaction time of 72 min and the results are shown in Table 1. In each case, the crosslinker EGDMA was consumed more rapidly than the monomers MA or MMA. There was one common formulation, 10%*T* and 15%*C*, that gave high molecular weight soluble polymers for both MA/EGDMA and MMA/EGDMA systems. Hence this was further investigated by following the kinetics of polymerization, as shown in Fig. 3. The consumption of EGDMA was found to be similar in both MA/EGDMA and MMA/EGDMA systems at this formulation. Also, EGDMA was again consumed more rapidly than both MA and MMA, with its conversion reaching 100% in about half an hour. The reactivity ratios for the copolymerization of MA and MMA have been reported to be 0.55 and 1.67, respectively [33]. The reactivity of the vinyl functional group for the methacrylate monomer MMA and the methacrylate crosslinker EGDMA can be considered as a first approximation to be dependent on the functionality of the end group and, therefore, assumed identical. Thus, at the initial stages of the reaction ($\leq$10 min), the rate of consumption of EGDMA is 5–6 times faster than MA due to higher reactivity of the methacrylate type double bond on EGDMA than the acrylate type on MA. On the other hand, the rate of consumption of EGDMA is approximately doubled that of MMA, allowing for each one reactive double bond on MMA per two reactive double bonds on EGDMA and similar reactivities of methacrylate type double bonds on both the monomer and crosslinker. This trend was observed for other MMA/EGDMA formulations as well (10%*T*, 5%*C* and 15%*T*, 3%*C*), suggesting that this is solely a reactivity ratio effect rather than due to concentration differences. Data for the 10%*T* and 15%*C* formulation are summarized in Table 2.

Table 1
Monomer conversion for MA/EGDMA and MMA/EGDMA (different formulations; reaction temperature 100 °C; reaction time 72 min)

Formulation	% Monomer conversion		
	MA	MMA	EGDMA
MA/EGDMA 10%*T*, 15%*C*	63.4	–	99.7
MA/EGDMA 20%*T*, 8%*C*	83.7	–	99.1
MA/EGDMA 25%*T*, 4%*C*	85.6	–	99.4
MA/EGDMA 30%*T*, 1%*C*	92.1	–	98.0
MMA/EGDMA 10%*T*, 15%*C*	–	86.5	99.4

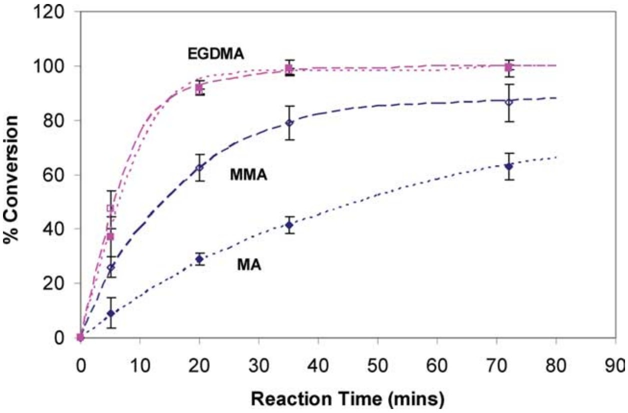

Fig. 3. Kinetics of polymerization for MA/EGDMA and MMA/EGDMA. Formulation 10%*T* and 15%*C*; temperature 100 °C; polymerization solvent *p*-xylene. Monomer conversion determined by GC–MS.

3.3. Molecular weight and intrinsic viscosity

Molecular weight and intrinsic viscosity data obtained from the GPC are plotted for MA/EGDMA and MMA/EGDMA polymers of different formulations, as shown in Fig. 4. Also included are precise MMA/EGDMA star microgels prepared by the 'controlled' polymerization technique ATRP and also linear poly(methyl methacrylate) (PMMA) standards purchased from Polymer Laboratories Ltd.

The molecular weight distributions of MA/EGDMA and MMA/EGDMA polymers were very broad due to the nature of the polymerization technique. However, some general trends could be seen. At low molecular weights ($<1\times10^5$ Da), there were little difference in intrinsic viscosity between the linear PMMA and the MA/EGDMA and MMA/EGDMA polymers. However, as the molecular weight increased ($>2\times10^5$ Da), the results started to diverge with the linear polymers increasing dramatically in intrinsic viscosity while the MA/EGDMA and

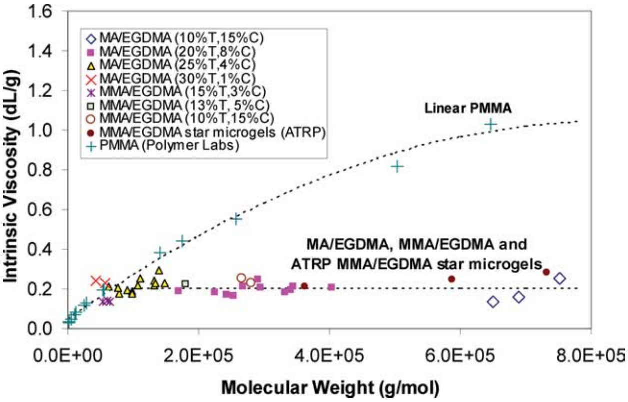

Fig. 4. Molecular weight versus intrinsic viscosity plot for MA/EGDMA and MMA/EGDMA polymers of different formulations prepared by free radical polymerization. Also shown are precise MMA/EDGMA star microgels prepared by ATRP method and linear PMMA from commercial sources. Data were obtained by GPC.

Table 2
Kinetics of polymerization for MA/EGDMA and MMA/EGDMA (formulation 10%*T* and 15%*C*)

t (min)	% Monomer conversion				
	MA	MMA	EGDMA	EGDMA/MA	EGDMA/MMA
0	0	0	0	–	–
5	8	25	45	5.6	1.8
10	15	40	75	5.0	1.9
15	22	52	88	4.0	1.7
20	28	62	93	3.3	1.5
25	33	70	95	2.9	1.4
30	38	75	97	2.6	1.3
40	45	82	99	2.2	1.2
50	52	85	99	1.9	1.2
60	58	86	100	1.7	1.2
70	63	87	100	1.6	1.1
80	66	88	100	1.5	1.1

MMA/EGDMA systems remained fairly constant. For example, at 6.5×10^5 Da, the intrinsic viscosity of linear PMMA was close to 1.0 dL/g while the MA/EGDMA polymer remained at approximately 0.2 dL/g. The lack of molecular weight dependence for the latter systems is indicative of a compact polymer structure where the polymer arms do not extend freely into the solvent and such behaviour has also been shown for precise star microgels prepared by 'controlled' polymerization techniques (e.g. Ref. [15]).

This comparison can also be seen clearly from the GPC traces in Fig. 5. While the three detector signals are of comparable intensities for the linear polymer, the differential pressure (DP) signal, corresponding to the intrinsic viscosity, is much smaller than the light scattering (LS) signal, or molecular weight, for the MA/EGDMA polymer. In addition, the narrow polydispersity of the linear PMMA is reflected in its sharp RI peak, in contrast to the broad peak for MA/EGDMA, representing the broad distribution of polymer products formed that is characteristic of the conventional free radical polymerization process.

3.4. Bulk solution viscosity

Bulk solution viscosities are perhaps a more important measure of the properties of the polymer solutions, as these directly affect the processability of the material in the applications they are intended for and provide information necessary for such engineering design purposes as pipe specifications and pump sizing. The rheological behaviour of the polymers formed in this work was explored by examining their flow curves under different conditions. The first point to note is that while flow occurred at 20 °C for MA/EGDMA and MMA/EGDMA polymers at low concentrations (<20% w/w), these polymers exhibited a high yield stress at higher concentrations (no rotation of the cone even at high shear stresses, e.g. up to 4 kPa). However, increasing the solution temperature to 25 °C completely removed this yield stress for all polymer formulations and concentrations tested. Hence, all subsequent experiments were performed and compared at this higher temperature.

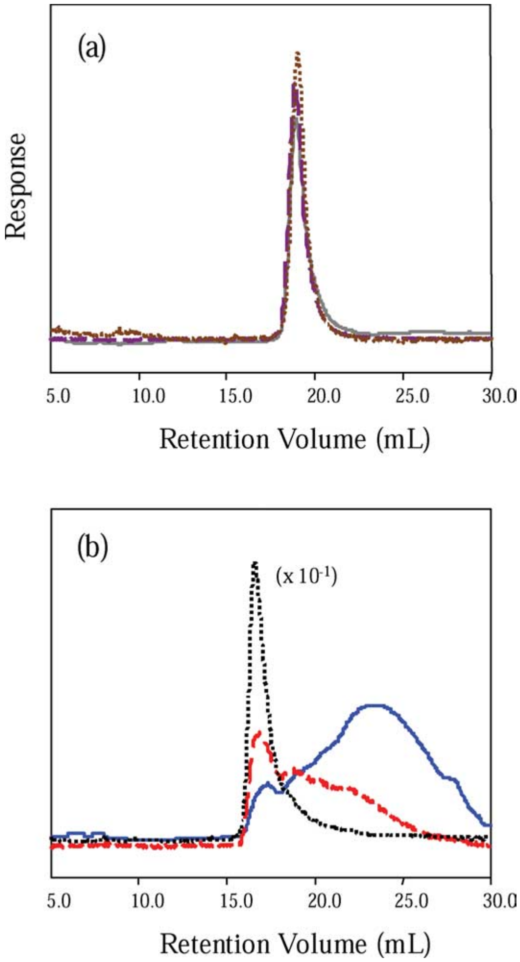

Fig. 5. GPC traces for (a) linear PMMA standard, $M_w=140{,}200$ Da; and (b) MA/EGDMA polymer, formulation 20%*T* and 8%*C*, $M_w=168{,}800$ Da. These diagrams show signals from the refractive index (solid lines), differential pressure (long dashes) and light scattering (dotted curves) detectors. The LS trace for the MA/EGDMA polymer has been scaled down 10-fold to show details of the RI and DP signals.

The change in flow behaviour with polymer concentration at the constant temperature of 25 °C was further observed and shown in Fig. 6. While the viscosity showed a lack of shear rate dependence over the entire shear rate range tested at low polymer concentrations (true Newtonian behaviour), a shear thinning behaviour was observed at higher polymer concentrations. This change in viscosity with shear rate is likely to be the result of re-orientation and re-alignment of the polymers in solution before steady state is reached.

The plots of bulk solution viscosity when steady state has been reached, versus the concentrations of MA/EGDMA and MMA/EGDMA polymers prepared by conventional free radical polymerization, are shown in Fig. 7(a) and (b). Data for a MMA/EGDMA star microgel prepared by the ATRP method [16] are also shown as reference. In all cases, the increase in viscosity is more pronounced at higher polymer concentrations as the interactions (entanglement) between individual polymers are more significant.

The bulk viscosities of the MA/EGDMA polymers are much lower than the ATRP MMA/EGDMA star microgels at concentrations above 30% w/w, as shown in Fig. 7(a). On the other hand, the MMA/EGDMA polymers have similar or higher viscosities than the star microgels over the same concentration range, as shown in Fig. 7(b). Hence it can be inferred that the MA/EGDMA system produced polymers that have lower viscosities than the MMA/EGDMA system, although the former was shown to have a wider molecular weight range that extended to the higher value end. This suggests that MA/EGDMA polymers are more branched, or star-like, in structure than the MMA/EGDMA polymers, as low bulk viscosities are characteristic of star polymers due to limited intermolecular chain entanglement.

The reason for the considerably lower viscosities of MA/EGDMA polymers compared to the precise star microgel prepared by ATRP could lie in their broad polydispersities. For the MA/EGDMA system, the high molecular weight star-like fraction should have rheological behaviour similar to that of the ATRP star microgels, while the low molecular weight fractions will generally be expected to show lower viscosities. The broad polymer distribution in this system will, therefore, cause an overall reduction in observed viscosity to that below the ATRP star microgel. For example, with an MA/EGDMA concentration of 50% w/w as shown in Fig. 7(a), it may be that only 30% w/w of this polymer solution has molecular weight above 500 kDa, with the rest of the solution made up of lower molecular weight polymers. Therefore, one is in effect comparing the contribution of this 30% of high molecular weight polymer to the overall solution viscosity, with all 50% of the ATRP star microgel having molecular weight 500 kDa. For the MMA/EGDMA system on the other hand, a similar amount of low molecular weight fraction should not contribute significantly to the overall reduction in bulk viscosity due to the narrower molecular weight range of the polymers formed. The observation of higher viscosities for this system must, therefore, be due to the fraction of higher molecular weight polymer being less branched, or less star-like, than the ATRP star microgels.

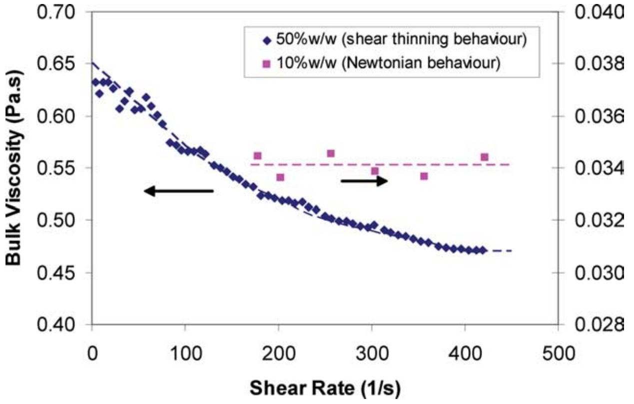

Fig. 6. Plot of bulk solution viscosity versus shear rate for MA/EGDMA polymer of formulation 20%T and 8%C, measured by cone-and-plate rheometry at 25 °C. Different flow behaviour is shown at different polymer concentrations.

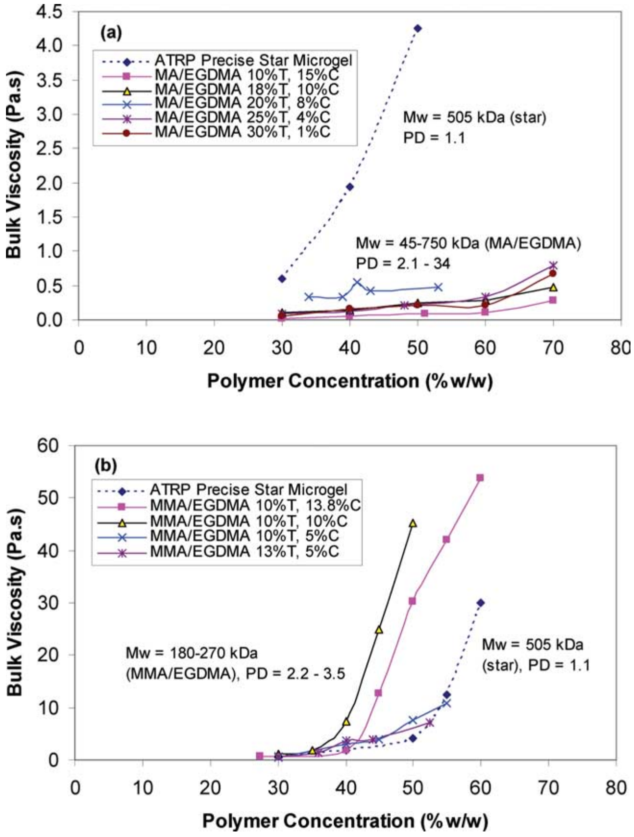

Fig. 7. Bulk viscosities of (a) MA/EGDMA and (b) MMA/EGDMA polymers prepared by free radical polymerization, in comparison with a precise star microgel prepared by ATRP. Results were obtained by cone-and-plate rheometry at 25 °C over a range of polymer concentrations.

One might argue if it is reasonable to compare the rheological behaviour of MA/EGDMA polymers with the ATRP MMA/EGDMA star microgels in the first instance, as the polymers are made of different monomeric components.

For this we examine the intrinsic viscosity versus molecular weight relationship for the homopolymers poly(methyl acrylate) (PMA) and poly(methyl methacrylate) (PMMA). The Mark–Houwink equation states that the relationship between the intrinsic viscosity [η] and the molecular weight (M_W) of a linear polymer is such that $[\eta]=K(M_w)^a$, where K and a are constants that depend on polymer-solvent interactions. To our knowledge no data exist for PMA and PMMA in the solvent system that we have tested (*p*-xylene at 100 °C), but the closest system that can be used for comparison is toluene at 30 °C, where K and a are 7.79×10^{-3} mL/g and 0.697 for PMA and 7.00×10^{-3} mL/g and 0.710 for PMMA [34]. The intrinsic viscosity, which essentially reflects the capability of a polymer in solution to enhance the viscosity of the solution, is expected to diverge more significantly between the two types of polymers at higher molecular weights. Our calculations suggest that this difference is negligible even for our highest molecular weight polymers (750 kDa), where [η] is estimated to be 0.97 and 1.04 dL/g for PMA and PMMA, respectively. Therefore, the considerably lower bulk solution viscosities of MA/EGDMA than MMA/EGDMA polymers can be attributed to macromolecular structural differences rather than the nature of the monomers used.

Further comparison of rheological data is shown in Fig. 8 for a precise star microgel, a MA/EGDMA star-like microgel, and a linear PMMA polymer of comparable molecular weights. The linear polymer exhibits the highest solution viscosity and the entanglement occurs at much lower concentrations, as expected.

3.5. Polymer architecture

The different rheological behaviour for the MA/EGDMA and MMA/EGDMA polymers formed by free radical polymerization have been shown in this work to be due to different microgel network structures formed. Patras et al. [35] demonstrated with hydrogel films (electrophoresis gels) that the aqueous free radical polymerization between monomer acrylamide (AAm) and crosslinker *N*,*N*′-methylenebis(acrylamide) (Bis) yielded a statistical polymeric network with relatively even crosslinking density and high degree of homogeneity due to similar reactivities of AAm and Bis. However, the reaction between AAm and a more reactive crosslinker *N*,*N*′-methylenebis(methacrylamide) (mBis) resulted in a heterogeneous network consisting mainly of linear chains branching away from highly crosslinked loci. Similar, though less pronounced, observations were made between AAm and 1,3,5-triacrylylperhydro-*s*-triazine (similar reactivity, statistical network) in contrast to that between AAm and 1,3,5-trimethacrylylperhydro-*s*-triazine (different reactivity, heterogeneous network). The reactivity ratio of methacrylamide type double bonds over the acrylamide ones has been reported to be approximately 1.35 [36].

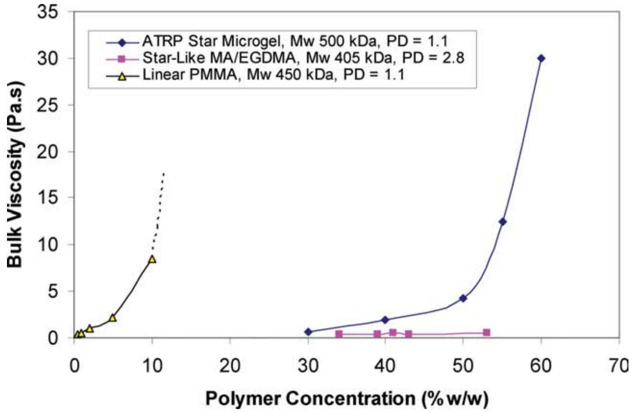

Fig. 8. Bulk viscosities of a precise star microgel prepared by ATRP method, a star-like MA/EGDMA microgel prepared by free radical polymerization, and a linear PMMA polymer obtained from Polymer Laboratories Ltd, all of comparable molecular weights.

The same concept can be applied to the acrylate/methacrylate systems here. MA has been reported to be less reactive than MMA [33], while MMA and EGDMA have been assumed to be similar in reactivity ratio and this has also been confirmed from conversion data presented in Fig. 3. Thus in the present work, the more reactive divinyl monomer EGDMA will tend to react preferentially with more EGDMA, leading initially to a large proportion of crosslinking loci. As the amount of EGDMA becomes depleted, polymerization of the mono-vinyl MA starts to occur with linear arms adding to any unreacted pendant double bonds in the EGDMA loci. The result is a highly branched polymer with a relatively dense core and multiple arms radiating from the core. Fig. 9 gives a schematic illustration of the star-like microgel formation. The initially formed loci (Fig. 9(b)) will provide unreacted pendant double bonds after EGDMA is incorporated into the polymer. Linear polymer subsequently grows through these pendant double bonds, which forms the branched arms of star-like microgels. We have attempted to measure these pendant double bonds by NMR for the samples after reaction of 10 and 40 min. NMR observed no signals due to pendant double bonds. This observation is similar to that reported for precise star microgels [16], where the immobility of the crosslinked core caused the signals of pendant double bonds to be broadened into the NMR baseline.

The reaction between MMA and EGDMA will result in the formation of a more homogeneous network structure as both components react in a more statistical manner. The core-arm, or star-like, structure of MA/EGDMA thus behaves as discrete ‘colloidal’ particles giving rise to lower solution viscosities, whereas the MMA/EGDMA behaves more like a statistical network with higher solution viscosities, but not to the extreme of high molecular weight linear polymers.

Recently, Sherrington’s group in the UK reported a one-pot synthesis of branched vinyl polymers via conventional free radical polymerization using chain transfer agent [37].

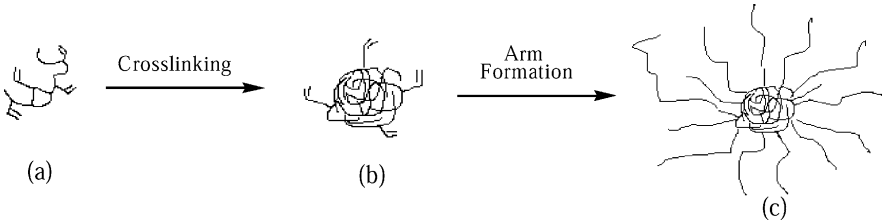

Fig. 9. Schematic illustration of the formation of star-like microgels.

The material produced is complementary to the star-like microgel reported here. Combination of the two could yield a more versatile product.

4. Conclusions

Polymers were synthesized by conventional free radical polymerization. Two systems were studied: methyl acrylate (MA) or methyl methacrylate (MMA) crosslinked with ethylene glycol dimethacrylate (EGDMA). Low molecular weight oligomers, high molecular weight soluble polymers, or insoluble gels may be obtained depending on the ratio and total concentration of monomer and crosslinker.

The high molecular weight soluble polymers were further characterized by gas chromatography-mass spectrometry (GC–MS), gel permeation chromatography (GPC), and cone-and-plate rheometry. Monomer conversion data obtained from GCMS confirmed the initial hypothesis of lower reactivity of MA but similar reactivity of MMA to the crosslinker EGDMA (lower reactivity of acrylate type double bonds compared to methacrylate type double bonds). GPC data indicated that both MA/EGDMA and MMA/EGDMA systems showed low and similar intrinsic viscosities (≈ 0.2 dL/g) which were essentially independent of their molecular weight. On the other hand, cone-and-plate rheometry revealed the structural differences between the two types of polymers, with the star-like MA/EGDMA polymers having lower bulk solution viscosities than the more statistical MMA/EGDMA polymers. These polymers in turn have much lower intrinsic as well as bulk viscosities than linear polymers of comparable molecular weight.

Thus, by exploiting differences in monomer and crosslinker reactivity, it is possible to produce polymers that can mimic the precise star microgels possessing the same desirable mechanical and rheological properties (high molecular weight, low bulk viscosity) as those obtained from ‘controlled’ polymerization techniques but without the high costs and processing difficulties that are currently limiting their scaled-up production. These features make the conventional free radical polymerization methodology attractive in various industrial applications such as reducing solvent use and, therefore, emission of volatile organic carbons in paints and coatings formulations.

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