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Studies on microgels: 2. Analysis of the reaction between 'living' poly(4-t-butylstyrene) and dimethacrylates by size exclusion chromatography coupled with d.r.i., u.v. and m.a.l.l.s. detectors

Ludger Pille, Akhil G. Jhingran, Evamarie P. Capareda* and David H. Solomon†
School of Chemistry, University of Melbourne, Parkville, VIC 3052, Australia
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The reaction between 'living' poly(4-t-butylstyrene) [P(tBS)], and the dimethacrylates ethylene glycol dimethacrylate (EGDMA) and 1,4-butanediol dimethacrylate (BDDMA) was analysed by size exclusion chromatography equipped with a differential refractive index (d.r.i.), an ultraviolet (u.v.) and a light scattering detector (l.s.). The information obtained by the d.r.i. and u.v. detectors allowed the calculation of the concentration of 4-t-butylstyrene and dimethacrylate along the size exclusion chromatogram. The l.s. detector allowed the estimation of molecular weight as a function of the elution volume V_e. The combined information from the detectors led to the conclusion that the reaction produced lightly branched P(tBS) and microgel polymers. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The evaluation of copolymer composition is normally done on the bulk sample by conventional methods such as n.m.r., i.r. or u.v. spectroscopy and elemental analysis. This approach assumes that the monomer distribution in polymers is homogeneous, which is not necessarily always the case. In non-ideal radical copolymerizations for example, different monomer sequence lengths in the polymer can be observed[1].

Size exclusion chromatography (s.e.c.) is the most widely used method to fractionate macromolecules. The underlying principle in s.e.c. is the separation of hydrodynamic volumes[2]. The monomer composition in individual s.e.c. fractions can be determined by using detectors that are sensitive to individual monomers. For example, Zimina *et al.* used a u.v. diode-array detector to analyse the monomer ratio of a poly(styrene-*b*-methyl methacrylate) block copolymer along the size exclusion chromatogram[3], and Burgess *et al.* used a combination of u.v. and differential refractive index (d.r.i.) detectors to determine the composition of a poly(styrene-*b*-tetrahydrofuran) block copolymer as a function of elution volume[4].

We report here the analysis of the reaction between 'living' poly(4-t-butylstyrene) and dimethacrylates by s.e.c. equipped with differential refractive index (d.r.i.), ultraviolet (u.v.) and multi-angle laser light scattering (m.a.l.l.s.) detectors. Crosslinked soluble polymer molecules, which are called microgels, are formed in this reaction. These polymers have been the focus of some research in the recent past because of their interesting architectural nature[5–13].

This reaction is to our knowledge the first reported microgel formation between 'living' hydrophobic macromolecules and hydrophilic multifunctional monomer.

EXPERIMENTAL

All work was carried out under strict argon atmosphere (99.99%).

Materials

4-t-Butylstyrene (tBS) was commercially obtained from Polysciences Inc. It was dried over CaH_2 and twice distilled under reduced pressure (b.p. = 91°C at 9 mm Hg).

Ethylene glycol dimethacrylate (EGDMA) and 1,4-butanediol dimethacrylate (BDDMA) were obtained from Aldrich Chemicals. Both monomers were dried over CaH_2 and twice distilled under reduced pressure ($b.p._{EGDMA}$ = 50°C at 1 mm Hg, $b.p._{BDDMA}$ = 75°C at 1 mm Hg). Distillation of the monomers over triethylaluminium, which is the most widely used method for the purification of acrylates[14], failed. Triethylaluminium initiated the polymerization of the monomers at room temperature.

* On leave from: Institute of Chemistry, University of Philippines, Philippines 4031
† To whom correspondence should be addressed

Tetrahydrofuran (THF) was refluxed over sodium and benzophenone until a deep blue colour appeared. Prior to use it was distilled onto a poly(styryllithium) solution and refluxed for a further hour.

Lithium chloride (99+%) was obtained from Aldrich Chemicals and dried overnight at 110°C under vacuum.

Polymerization

All the glassware and syringes used were kept overnight in an oven at 120°C. A two-necked round-bottomed flask containing a magnetic bar stirrer and LiCl (~ 7 mg) was flamed dried three times under vacuum and each time flushed with argon. THF (50 ml) was introduced through a syringe into the round-bottomed flask and cooled to −90°C. The required amount of t-BuLi solution was transferred slowly via a syringe into the rapidly stirred solution, followed by the addition of tBS. The colour of the reaction mixture changed to deep orange, indicating the start of the reaction. A sample (~ 5 ml) of the 'living' polymer was taken after 1 h and quenched with methanol.

The crosslinker (EGDMA or BDDMA), was then added to the vigorously stirred living poly(tBS) solution. The colour of the solution changed to pale yellow. The reaction was allowed to proceed for a further hour at −90°C, before being quenched with methanol. The copolymer was precipitated in methanol, filtered and dried in vacuum.

Characterization

A series of two 10^3 Å, two 10^4 Å and one 10^5 Å Ultrastyragel columns from Waters was used for the fractionation of the polymers. A differential refractometer (Waters model 410) operating at 933 nm, a tunable ultraviolet detector (Waters model 486) and a multi-angle laser light scattering instrument (Dawn F from Wyatt Technology Corporation) operating at 632.8 nm were used as on-line detectors. Untreated h.p.l.c.-grade THF was used as mobile phase and pumped at a flow rate of 1 ml min^{-1}.

The data from the differential refractometer and the ultraviolet detector were collected with the Baseline software package from Waters. The light scattering data were collected and analysed with the Astra and Easi software packages from Wyatt Technology Corporation.

Unsaturation in the polymers was determined with a *FT*i.r. spectrometer from Biorad (model FTS-60A).

SIZE EXCLUSION CHROMATOGRAPHY WITH DIFFERENT DETECTORS

We have examined the copolymers by size exclusion chromatography coupled to a differential refractive index (d.r.i.), ultraviolet (u.v.) and multi-angle laser light scattering (m.a.l.l.s.) detector. Each of these detectors provides different information about the copolymer.

Differential refractive index (d.r.i.) detection

The refractive index increment dn/dc is a unique constant for a given solvent–polymer system, expressing the linear correlation between the refractive index and the concentration of a polymer in a given solvent. The dn/dc of copolymers is a function of the refractive index increments of the homopolymers:

$$(dn/dc)_{co} = w_A(dn/dc)_A + w_B(dn/dc)_B \quad (1)$$

Here the subscripts A and B denote the two homopolymers, co is the copolymer and w is the weight fraction of specified monomer unit in the copolymer.

The d.r.i. detector shows the change of the refractive index Δn along the chromatogram, which in our case is the combined response from the dimethacrylate and poly(tBS).

The refractive index increment of a polymer sample can be extracted from the s.e.c.–d.r.i. chromatogram if one assumes that all polymer is eluted from the columns and that the refractive index increment is homogeneous throughout the sample. The concentration $(\Delta c_i)_{dri}$ and refractive index change Δn_i at each slice can then be expressed by:

$$(\Delta c_i)_{dri} = \frac{m_i}{\Delta V_i} = \frac{m_0}{\Delta V_i}\frac{I_i}{\sum_{peak} I} \quad (2)$$

$$\Delta n_i = \alpha I_i \quad (3)$$

with $\Delta V_i = V_{i+1} - V_i$. Here m_i, ΔV_i and I_i are the mass, volume and d.r.i. detector response at the ith slice respectively; m_0 is the total injected mass; α is the constant converting the d.r.i. detector response into refractive index units; and V_{i+1} and V_i are the elution volume at slice i and $i + 1$.

Division of equation (3) by equation (2) yields $\Delta n_i/\Delta c_i$, which is the dn/dc for the polymer:

$$\frac{\Delta n_i}{\Delta c_i} = \frac{\Delta V_i \alpha \sum_{peak} I}{m_0} = \frac{dn}{dc} \quad (4)$$

The constant α was determined through the calibration of the d.r.i. detector with standards of known refractive index increment (polystyrene) by applying the 'flow injection analysis (f.i.a.). This involves the injection of samples through the injector directly into the detector, thus bypassing the columns.

It is assumed that the sample running through the detector in the first couple of moments is not diluted by the carrier solvent. *Figure 1a* shows the calibration curve, from which $\alpha = 4.28 \times 10^{-5}$ RIU/V was determined. The validity of this approach was tested by comparing the injected mass of s.e.c. runs with the calculated mass.

Ultraviolet (u.v.) detection

Figure 2 shows the u.v. spectra of poly(tBS), poly(methyl methacrylate) (PMMA) and EGDMA. It illustrates that neither PMMA nor EGDMA show any absorption at high wavelength. We assumed in this study that the absorption spectrum of PMMA is a model for the absorption spectra of totally converted EGDMA or BDDMA, and that the absorption spectrum of EGDMA is a model for pendant double bonds in microgels. The s.e.c. chromatogram detected at 271 nm will therefore only show the contribution of poly(tBS) in the copolymer. The u.v. detector response can be quantified if the Beer–Lambert law is obeyed:

$$(\Delta c_i)_{uv} = \beta U_i \quad (5)$$

Here $(\Delta c_i)_{uv}$ and U_i are the concentration of the polymer and the response of the u.v. detector at the ith slice; and β converts the u.v. response into concentration. The total

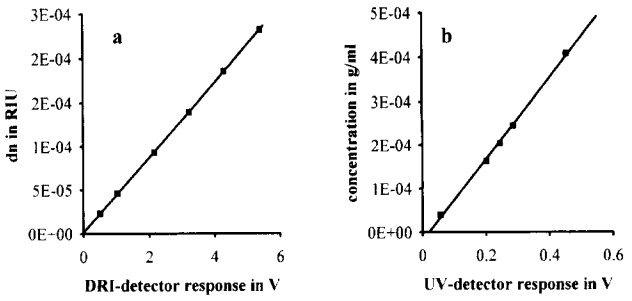

Figure 1 Calibration curves for the differential refractive index detector (a) and the ultraviolet detector (b). Polystyrene was used for the calibration of the differential refractive index detector and poly(tBS) for the calibration of the ultraviolet detector (271 nm)

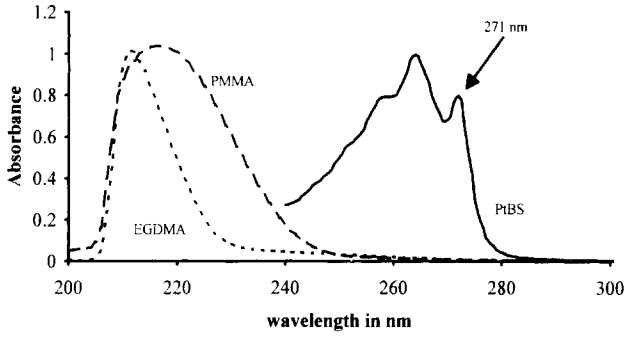

Figure 2 The u.v. absorption spectra of PMMA, EGDMA and poly(tBS)

mass of poly(tBS) in the polymer sample can then be calculated:

$$m_{\mathrm{tBS}} = \sum_{\mathrm{peak}} (\Delta c_i)_{\mathrm{uv}} \Delta V_i \tag{6}$$

Figure 1b shows the calibration curve obtained for the u.v. detector through f.i.a. of poly(tBS), from which $\beta = 9.26 \times 10^{-3}$ g/ml V was determined.

Light scattering (l.s.)

Conventional molecularweight determination in size exclusion chromatography is based on comparison of hydrodynamic volumes[2]. Absolute molecularweight detection such as light scattering is required for the analysis of polymers for which no standards of the same chemistry and architecture are available. This is generally the case for branched and crosslinked polymers.

The same basic equations as used in common light scattering measurements can be applied for every slice along the chromatogram if the light scattering instrument is used as on-line instrument for s.e.c.[16].

$$\frac{R(\theta)_i}{K \Delta c_i} = M_{\mathrm{w},i} P(\theta)_i - 2A_{2i} \Delta c_i M_{\mathrm{w},i}^2 P(\theta)_i^2 \tag{7}$$

Here $R(\theta)$ is the excess Rayleigh ratio, K is an optical constant, c is the concentration, M_{w} is the weight-average molecular weight, $P(\theta)$ is the particle scattering factor and A_2 is the second virial coefficient. The subscript i indicates the measurement at slice i of the chromatogram. It is important to notice that the refractive index increment $\mathrm{d}n/\mathrm{d}c$ is part of the optical constant K:

$$K = 4\pi^2 n^2 (\mathrm{d}n/\mathrm{d}c)^2 / \lambda^4 N_{\mathrm{A}} \tag{8}$$

Here n is the refractive index of the solvent, λ is the wavelength of the incident light and N_{A} is the Avogadro number.

$P(\theta)$ in equation (7) is equal to 1 at $\theta = 0$ and since in s.e.c. $2A_2 M_{\mathrm{w}} c \ll 1$, equation (7) simplifies to:

$$\frac{R(\theta)_i}{K \Delta c_i} = M_{\mathrm{w},i} \tag{9}$$

Please note that the intensity of the light scattered is proportional to the concentration multiplied by the molecular weight.

The overall weight-average molecular weight of the polymer sample $\overline{M}_{\mathrm{w}}$ is then calculated through:

$$\overline{M}_{\mathrm{w}} = \frac{\sum_{\mathrm{peak}} \Delta c_i M_{\mathrm{w},i}}{\sum_{\mathrm{peak}} \Delta c_i}$$

RESULTS AND DISCUSSION

Figures 3 and *4* show the s.e.c. chromatograms of the microgel samples B254 and E534 recorded with the d.r.i., u.v. and l.s. detectors and the s.e.c.–d.r.i. trace of the respective precursor poly(tBS) arms. The prefixes B and E denote microgels containing 1,4-butanediol dimethacrylate (BDDMA) and ethylene glycol dimethacrylate (EGDMA) respectively.

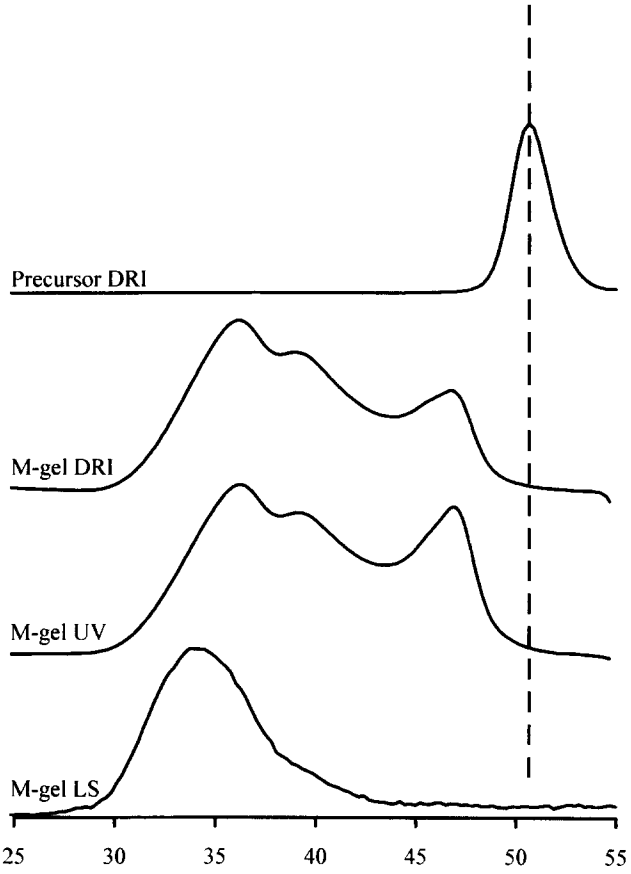

Figure 3 Size exclusion chromatograms of B254 detected with the differential refractive index detector, ultraviolet detector (271 nm) and light scattering detector. The top chromatogram is of the 'living' poly(tBS) arms before the crosslinking reaction

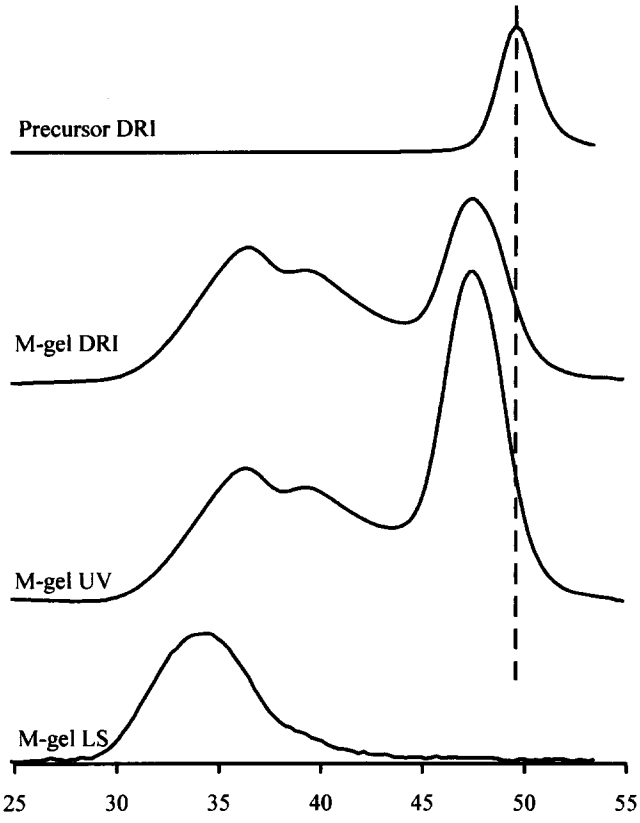

Figure 4 Size exclusion chromatograms of E534 detected with the differential refractive index detector, ultraviolet detector (271 nm) and light scattering detector. The top chromatogram is of the poly(tBS) arms before the crosslinking reaction

Table 1 Refractive index increments of microgel and polymerized crosslinker and weight fraction of poly(tBS) in polymer[a]

Sample	$(dn/dc)_{m\text{-}gel}$ ($ml\,g^{-1}$) s.e.c.–d.r.i.	$(dn/dc)_{cross}$ ($ml\,g^{-1}$) eqn (1)[b]	Poly(tBS) (wt%) s.e.c.–u.v.	Poly(tBS) (wt%) expt[c]
B544	0.132	0.98	81	83
B554	0.126	0.101	64	73
B254	0.126	0.105	60	69
E144	0.131	0.096	80	82
E534	0.126	0.103	62	65
E634	0.120	0.099	51	58

[a] The subscripts m-gel and cross denote microgel and poly(BDDMA) or poly(EGDMA) respectively
[b] Values were obtained through equation (1) by assuming $(dn/dc)_{poly(tBS)} = 0.140\,ml\,g^{-1}$
[c] The weight fraction poly(tBS) used in the experiment

Table 1 shows the refractive index increments and weight fraction of tBS in the microgel samples which were obtained through the application of equations (5) and (6). It also shows the weight fraction of tBS used in the reaction. The calculated and used amounts deviate by up to 10%. This compares well with the work of Zimina *et al.*, who used a u.v. diode array detector to examine polystyrene–poly(methyl methacrylate) block copolymers. They found that the n.m.r. results showed up to 16% more polystyrene[3]. The amounts calculated from u.v. experiments performed on the bulk sample deviated only up to 7% from the weighed tBS fractions.

With the above information, it is now possible to

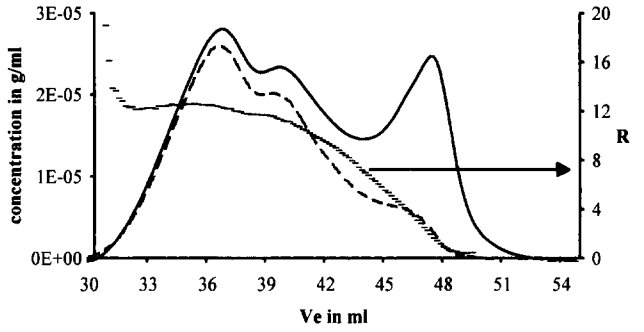

Figure 5 The concentration of poly(BDDMA) (- - - -), poly(tBS) (——) and the ratio *R versus* the elution volume V_e for B254

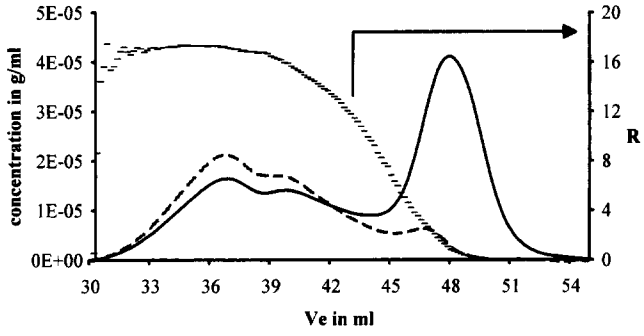

Figure 6 The concentration of poly(EGDMA) (- - - -), poly(tBS) (——) and the ratio *R versus* the elution volume V_e for E534

calculate (equation (1)) the refractive index increment of poly(EGDMA) and poly(BDDMA) assuming that the refractive index increment of poly(tBS) is $0.140\,ml\,g^{-1}$ (refs 6, 17). It should be mentioned here that the reported dn/dc for poly(tBS) were measured at room temperature and with light sources operating at 933 nm[6] and 632.8 nm[17]. This indicates that the dn/dc of poly(tBS) is independent of the wavelength of the light used. The refractive index increments of poly(EGDMA) and poly(BDDMA) thus calculated are between 0.096 and $0.105\,ml\,g^{-1}$. Note that we used the poly(tBS) weight fraction determined by s.e.c.–u.v. for the calculation. For subsequent calculations we have used a value of $0.100\,ml\,g^{-1}$ for both poly(EGDMA) and poly(BDDMA).

Both the u.v. and d.r.i. chromatograms of the microgel show multimodal distributions. Comparison with the s.e.c.–d.r.i. traces of the precursor indicates that the peak at high elution volume is not due to unreacted poly(tBS) arms since this peak is shifted towards higher molecular weights. Comparison of the d.r.i. with the u.v. chromatogram shows that the microgel samples are heterogeneous in their chemical composition. The peak at high elution volume in the u.v. trace is very intense, which indicates considerable poly(tBS) in this region. If the distribution of tBS in the microgel sample were homogeneous throughout the whole sample, the same relative intensities would have to be observed in the d.r.i. chromatogram. This is not the case.

The concentration of the crosslinker at each slice along the s.e.c. trace can be calculated from the d.r.i. and u.v. chromatograms. The refractive index change $(\Delta n_i)_{co}$ of the copolymer at each slice is the combined refractive index change from poly(tBS) and the

crosslinking agent:

$$(\Delta n_i)_{co} = (\Delta n_i)_{cross} + (\Delta n_i)_{poly(tBS)} \quad (10)$$

Rearrangement of this equation and substitution with equations (3), (4) and (5) leads to the concentration of the crosslinking agent at each slice along the chromatogram:

$$(\Delta c_i)_{cross} = \frac{\alpha I_i - \beta U_i (dn/dc)_{poly(tBS)}}{(dn/dc)_{cross}} \quad (11)$$

Figures 5 and *6* show the concentration of the poly(tBS), the crosslinking agent and the mole ratio:

$$R = \frac{[\text{crosslinking agent}]}{[\text{poly(tBS)}]}$$

along the s.e.c. chromatogram for the microgel samples B254 and E534. These figures clearly illustrate the heterogeneous character of the microgel sample. The peak at high elution volume contains much less crosslinking agent than the rest of the chromatogram. A minimum of $R = 0.5$ is required to link at least two poly(tBS) arms. It can be seen that in B254 R never drops below 0.5, whereas in the case of E534 the ratio drops below 0.5 only beyond the maximum of the peak at high elution volume. This explains the shift of this peak compared to the precursor peak, since most of this material consists of multiple poly(tBS) arms.

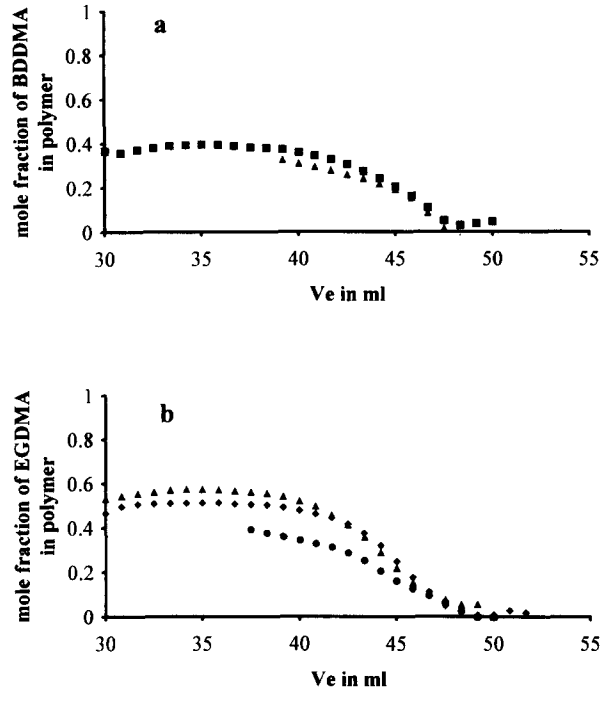

Figure 7 Mole fraction of (a) BDDMA (■ = B254, B554; ▲ = M544) and (b) EGDMA (● = E144; ◆ = E534; ▲ = E634) in polymer *versus* elution volume V_e

Table 2 Molecular weight of microgel and precursor poly(tBS) and the amount of unreacted double bonds

Sample	Microgel M_w (10^{-5} g mol^{-1})	Precursor poly(tBS) M_w (10^{-3} g mol^{-1})	Unreacted double bonds (%)
B544	0.23	2.9	1
B554	0.75	2.7	0
B254	2.54	2.9	0
E144	0.25	3.9	0
E534	1.79	2.6	9
E634	8.48	3.2	24

Figures 7a and *7b* show the mole fraction of poly(EGDMA) and poly(BDDMA) in the fractionated microgel sample. Each sample shows the same heterogeneous characteristics in that the mole fraction of the crosslinking agent drops sharply towards higher elution volume. It is remarkable that these polymers contain up to 60% of crosslinking agent.

Since the l.s. signal is proportional to the product of molecular weight times concentration, it is apparent that the peak at high elution volume does not contribute a great deal to the molecular weight of the microgel sample. The light scattering instrument does not show any response in the region of this peak.

The information obtained from the three detectors leads to the conclusion that the peak at high elution volume is due to very lightly branched poly(tBS) arms, where just a few molecules of the crosslinking agent are functioning as linking points for poly(tBS).

It is well known that the anionic polymerization of acrylates is prone to side reactions with the carbonyl group of the ester, which leads to deactivation of the active sites[18]. This could explain the presence of low-molecular-weight material in the chromatograms.

The addition of 1,1-diphenyl ethylene (DPE) to non-polar 'living' anions as an intermediate step in the copolymerization of non-polar and polar monomers[19] has been shown to reduce the side reactions in the polymerization of methyl methacrylate, t-butyl methacrylate, n-butyl methacrylate and t-butyl acrylate[20]. We have found that this intermediate addition of DPE did not show any change in the overall s.e.c.–d.r.i. trace in our experiments. We have therefore not used DPE in subsequent polymerizations, since every step in the anionic polymerizations is a possible source for impurities.

We suspect that remaining impurities in the acrylate monomers are mostly responsible for the side reactions. We are currently investigating methods other than distillation over triethylaluminium for the purification of the dimethacrylates.

Table 2 shows the molecular weight of the microgels, the molecular weight of the precursor poly(tBS) arms and the amount of unreacted double bonds.

The amount of unchanged double bonds was determined by *FT*i.r. It is interesting to note that the microgels containing BDDMA do not have any remaining unsaturation, whereas up to 24% of the double bonds have not reacted in the samples containing EGDMA. An explanation for the difference could be that the longer carbon chain between the double bonds in BDDMA make the polymer more flexible between the crosslinks, which should make the double bonds more accessible to nucleophilic attack. Light scattering of copolymers yields an apparent weight-average molecular weight $M_{w,app}$ due to the differences in refractive index increments of the individual molecules. In the case of a homogeneous distribution of the composition in the copolymer it is expected that the true molecular weight M_w will approach $M_{w,app}$[21].

Since the change of the refractive index, the concentration of tBS and the crosslinking agent at each point along the chromatogram are known, it is possible to calculate the refractive index increment for each point in

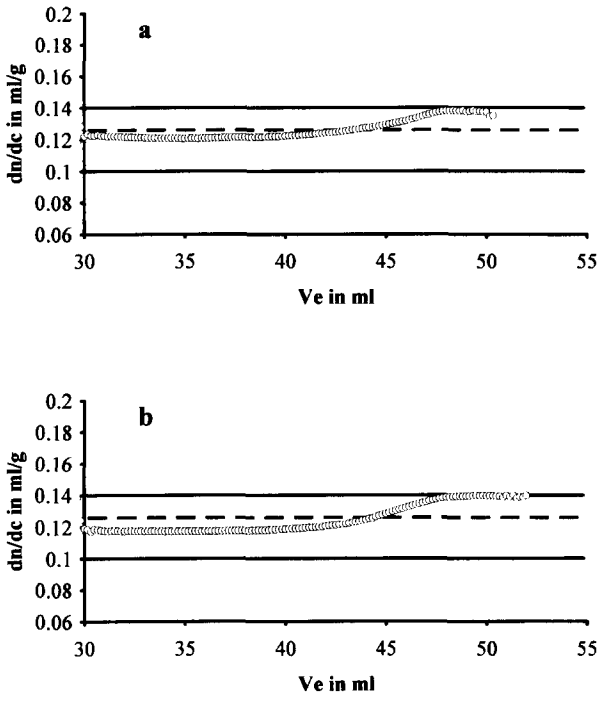

Figure 8 Plots of dn/dc of B254 (a) and E534 (b) *versus* elution volume V_e. Full lines represent the dn/dc of poly(tBS) and poly(EGDMA) or poly(BDDMA). The dashed line represents the dn/dc of the bulk sample

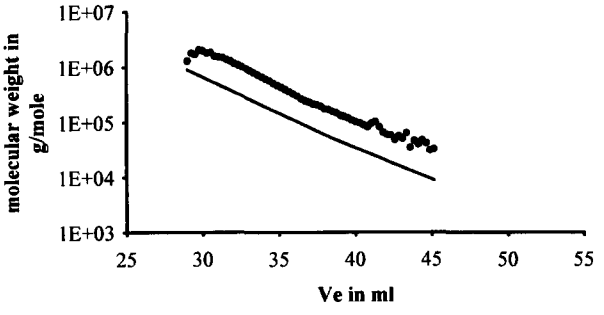

Figure 9 Molecular weight *versus* elution volume V_e for B254 and linear polystyrene

the chromatograms. This is shown in *Figures 8a* and *8b* for B254 and E534 together with the refractive index increment of poly(tBS), poly(EGDMA) and the refractive index increment of the bulk sample. It can be seen that the refractive index increment is constant over a large part of the chromatogram, which indicates a homogeneous distribution of the monomers in this region. It is approaching $0.140\,ml\,g^{-1}$ at high elution volume, where the lightly branched poly(tBS) elutes.

The molecular weights reported in *Table 2* have not taken the change of the refractive index increment into account. Here we used the refractive index increments of the bulk sample (*Table 1*) to calculate the molecular weights at each slice. This is justified since the macromolecules eluting in the region where the refractive index increment changes to $0.14\,ml\,g^{-1}$ do not contribute much to the overall weight-average molecular weight. However, the molecular weights reported in *Table 2* may be slightly in error since the dn/dc and the scattered light have been measured with light of different wavelength.

It was pointed out earlier that the underlying principle of size exclusion chromatography is the separation of hydrodynamic volumes[2]. Branched or crosslinked molecules have a much higher molecular weight at equivalent hydrodynamic volumes. This compact nature of the microgel samples can be demonstrated by plotting the molecular weight *versus* the elution volume for the microgels. *Figure 9* shows this plot for B254 as a representative for all microgels and linear polystyrene. The highly compact nature of the microgels is clearly demonstrated by the fact that their molecular weight at equivalent hydrodynamic volume (= elution volume) is much higher than the molecular weight of the linear polystyrene.

CONCLUSIONS

A comprehensive analysis of the reaction between living poly(tBS) and dimethacrylates was achieved by size exclusion chromatography coupled with d.r.i., u.v. and l.s. detectors. It was shown that the distribution of the crosslinking agent in the polymer sample is quite heterogeneous. The macromolecules with small amounts of crosslinking agent do not contribute a great deal to the overall molecular weight of the microgel samples. This leads to the conclusions that the samples consist of highly compact microgel molecules and lightly branched low-molecular-weight oligomers of poly(tBS).

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