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Polymer 43 (2002) 245–254

polymer

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Branched methacrylate copolymers from multifunctional monomers: chemical composition and physical architecture distributions

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Received 10 June 2001; received in revised form 14 August 2001; accepted 19 August 2001

Abstract

Soluble, branched (meth)acrylic copolymers have been made via facile, one-step, batch solution polymerisations taken to high conversion. Methyl methacrylate has been copolymerised with a bifunctional monomer using a chain transfer agent to inhibit gelation. Conventional chain transfer using a mercaptan has been compared to catalytic chain transfer (CCT) using a cobalt porphyrin. The polymerisations have been monitored as a function of monomer conversion and the polymer prepared at high conversion has been fractionated across the molecular weight distribution. The polymerisations remain isotropic, with both the chemical composition and physical architecture distribution varying systematically as a function of monomer conversion and copolymer molecular weight. A mechanism for the polymerisation is proposed based on the experimental data. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Free-radical polymerisation; Branched architecture; (Meth)acrylic polymers

1. Introduction

Though in principle there is a wealth of molecular architectures with which polymers may be formed, in practice most synthetic macromolecules that are exploited technologically are either linear species or crosslinked networks [1]. Other architectures are accessible, but generally, these require careful synthesis. Likewise, there are a wide variety of methods that can be used to make branched polymers but many of these are complex. Typically, these procedures require at least a two-step process in which a precursor is made first and then this is used to form branches in a second step (e.g. grafting from a backbone or copolymerisation of macromonomers) [2].

In the last 10 years there has been much interest in the synthesis of hyperbranched polymers [3–5]. These can be made via a single step process in the case of step-growth polymers. The most common method is the polycondensation of an AB_n monomer where A and B can react with each other but not with themselves, producing a hyperbranched polymer and there are many examples of these. In contrast, facile routes to branched and hyperbranched addition polymers are rare. Self-condensing vinyl polymerisation (SCVP) was first reported by Frechet et al. [6] and uses a vinyl monomer which has a second functional group capable of initiating the polymerisation of other vinyl groups. Frechet and his co-workers first used a 'living cationic' propagation but have extended this to include 'group transfer' and 'living free-radical' processes [7]. More recently, Matyjaszewski has applied the principle of SCVP in atom transfer radical polymerisation (ATRP) [8]. This is a 'living'/controlled polymerisation which uses an organic halide as an initiator in the presence of a copper (I) catalyst. The monomers must possess a vinyl double bond and a second reactive group (usually a halogen), which can be reversibly activated and deactivated. Propagation can take place at either the double bond or the halogen, therefore producing a branch point and eventually a branched polymer. Useful as these routes are, they do require tailored vinyl monomers that are specifically functionalised to allow branching to occur. For making architectures such as star branched (meth)acrylate copolymers via ATRP, coupling or cross-linking occurs if the polymer concentration is too high, so realistically these structures can only be made at low conversion of monomer to polymer [9,10] making them difficult to exploit industrially.

To our knowledge, apart from the use of polyfunctional mercaptans [11], no facile and broadly applicable method for transforming simple routine vinyl monomers like

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PII: S0032-3861(01)00581-X

methacrylates to branched polymers has been reported to date. Additionally, relatively little work has been carried out on characterising these polymers in detail and investigating their physical properties. This largely results from the need for careful synthesis where the chemistry involved does not allow for convenient scale up; large quantities of appropriate materials for study are typically not available. Most of the published literature on hyperbranched polymers mention the difficulties in characterising the molecular architecture of these polymers and point out how molecular weights determined by conventional gel permeation chromatography (GPC) are inaccurate because the branched structures of the polymers make the use of linear standards inappropriate. The only properties that have been fully reported in the literature are their solubility in a range of solvents and their low solution viscosity [12]. Relationships between dilute solution viscosity and molecular weight have been determined for many hyperbranched systems and the Mark–Houwink constant α typically varies between 0.5 and 0.2 depending on the degree of branching [4,13–15]. However, to our knowledge, there are no detailed reports on the chemical and physical composition distribution in hyperbranched polymers. Investigations of the thermal behaviour of hyperbranched polymers have suggested that the glass transition (T_g) can be controlled by the nature of end groups, as a result of their high concentration [4,16–18]. Information on the mechanical properties of hyperbranched polymers is still very limited, although a few studies allude to poor mechanical properties resulting from the lack of chain entanglements [18,19].

Multifunctional monomers (MFM) are used to make crosslinked polymers. In free-radical polymerisation, usually the inclusion of only small amounts of MFM (fractions of a percent) are required to produce a crosslinked network. Depending on the level of dilution of the monomers the whole system undergoes macrogelation in the case of concentrated solutions, or microgelation under conditions of high dilution. Elegant work originally by Staudinger and Husemann [20], and more recently by Antonietti and Rosenauer [21] studying the styrene/divinyl benzene system, has mapped out the interface between networks (macrogel) and microgel. Indeed implicit in these works and others [22] is the concept that branched polymers are the precursors to the macroscopic crosslinked gels. It has been shown that even in very dilute solution polymerisation ($\leqslant$10% monomer), the gel point is reached at substantially less than 20% conversion of monomer to polymer. Not surprisingly, the synthesis of soluble branched polymers without the formation of crosslinked polymers has seemed impossible in free-radical batch copolymerisations of MFMs polymerised to high conversion. However, we have recently disclosed the concept of copolymerising MFM to make soluble branched polymers by using an appropriate concentration of chain transfer agent to prevent crosslinking [23]. This can be achieved via a truly facile one step free-radical polymerisation process taken to high conversion using raw materials that are readily available. Therefore, this provides a practical and highly convenient method for preparing large quantities of branched, vinyl polymers. In this paper, we provide further details of this system. The polymer architecture has been monitored as a function of monomer conversion and a polymer made at high conversion has been fractionated to study both chemical composition and physical architecture as a function of molecular weight within the final molecular weight distribution. The reaction requires chain transfer to prevent crosslinking and catalytic chain transfer (CCT) using cobalt complexes has been compared to conventional chain transfer using mercaptans.

2. Experimental

2.1. Synthesis of branched copolymer

Polymers were synthesised via batch solution polymerisation in an oil bath thermostatically controlled at 80°C. All materials were used as supplied without further purification. Monomers contained inhibitor but this was not removed before use (standard industrial practise). A 250 ml three-necked round bottom flask was fitted with a condenser and a nitrogen supply. Methyl methacrylate (0.15 mol MMA, supplied by Ineos Acrylics) and tripropylene glycol diacrylate (2.50×10^{-3} mol TPGDA, supplied by Aldrich) were dissolved in toluene (0.33 mol LAR grade, supplied by Aldrich) using dodecyl mercaptan (1.48×10^{-3} mol DDM, supplied by Aldrich) as chain transfer agent. The polymerisation was initiated using 2,2′azobisisobutyronitrile (9.15×10^{-4} mol Perkadox AIBN, supplied by Akzo Nobel Chemicals). The polymerisation was performed up to a time of 6 h with a continuous flow of nitrogen bubbling slowly through the solution. Aliquots were taken from the reaction mixture at various times, corresponding to different conversions of monomer to polymer. Solutions were cooled immediately and free-radical inhibitor (phenothiazine) was added. Conventional GPC was performed directly on this solution after dilution. For further characterisation, the copolymers were precipitated into *n*-hexane and dried in a vacuum oven overnight at 40°C.

Similar reactions were performed as above, replacing DDM with a CCT agent bis(borondifluorodimethylglyoximate) cobaltate (II) (CoBF, varying concentration supplied by DuPont), but using different reagent concentrations (see text for details).

2.2. Copolymer chemical composition

^{1}H NMR spectra of copolymers in $CDCl_3$ were recorded using a JEOL GSX400 spectrometer. The spectra were used to determine the overall copolymer composition by monitoring the copolymerised TPGDA acrylate ester chemical shift (broad band) centred at approximately 5.0 ppm ($-CH_2-\mathbf{CH}(CH_3)-O-$) compared to the copolymerised MMA methacrylate ester chemical shift at 3.6 ppm ($-COO-\mathbf{CH}_3$).

2.3. Molecular weight evaluation

Molecular weight was determined by both conventional and triple detector methods. A conventional Polymer Laboratories GPC system with $2 \times 10\ \mu m$ mixed B columns was used to determine number average molecular weight (M_n), weight average molecular weight (M_w) and the polydispersity (M_w/M_n) of the polymers. The aliquots obtained from the polymerisation were diluted in chloroform (7.5 mg of polymer solution/1 ml chloroform) and filtered through a 2 μm filter. Chloroform was used as the mobile phase with an infra-red detector fixed at $1695\ cm^{-1}$ and the instrument was calibrated with linear PMMA standards. Percentage conversion was calculated from the relative areas of the polymer and monomer peaks on the GPC chromatogram. After isolation, polymers were also analysed using triple detector GPC (TDGPC). The instrument employed was by Viscotek and incorporated a laser differential refractometer, a differential viscometer and a right angle laser light scattering photometer. The data acquisition and reduction software was Trisec Version 3, also by Viscotek. A styrene-divinyl benzene, mixed gel column from Polymer Standards Service (PSS) was used with chloroform as the eluent at a flow rate of $1.0\ ml\ min^{-1}$.

2.4. Evaluation of glass transition temperature, T_g

T_g data were determined using a Mettler Toledo differential scanning calorimeter calibrated with an Indium standard. 10 mg of polymer sample were weighed into an aluminium pan which was sealed, placed in the calorimeter and heated at 20 °C per minute using an empty reference pan. Samples were heated above T_g and cooled rapidly, with T_g being established from the second heating run.

2.5. Copolymer fractionation

In addition to characterising copolymers isolated at various times, a polymer sample made at high conversion was fractionated across its molecular weight distribution. The fractions were reanalysed to obtain detailed information on chemical and physical composition as a function of molecular weight. The fractionation was carried out using GPC. This method was chosen for speed and simplicity since only a few milligrams of fraction material were needed for subsequent analysis. A conventional analytical column was used, rather than a preparative scale column, since the latter are very expensive and require high delivery solvent pumps and special arrangements for collection and recovery of fractions. Column selection and availability in a working analytical laboratory is usually restricted. There is a much wider choice of analytical columns, which are less expensive and have a greater separating power but have the disadvantage of a much lower sample loading. However, this was overcome by combining the fractions resulting from many injections of the same solution on the same column using identical conditions. This was achieved by using a programmable autosampler capable of controlling a fraction collector and handling upwards of 120 injection cycles. The apparatus used here consisted of a Gilson 231-401 autosampler — dilutor combination with a handshake link to a Gilson FC203 fraction collector fitted with collection vials of approximately 35 ml capacity each.

The concentration of the master batch was made higher than is usual for analytical work. The eventual concentration ($25\ mg\ ml^{-1}$) was determined by evaluating the computed molecular weight distribution of the target polymer at different concentrations in analytical mode on the column that was to be used for the fractionation. At the chosen concentration, the distortion created was considered to be acceptable. The raw chromatogram was then examined to determine the timing of the collection band. The collection band was split into 14 slices of equal width even though this produced unequal weight fractions in proportion to the molecular weight distribution. Subsequent injections were timed such that the sample emerged just after the last impurity peak of the previous sample had cleared.

After determining the collection parameters, the chromatograph was converted to carry out the fractionation. The detector was removed from the flow path and replaced by the fraction collector which was programmed with the previously determined operational parameters. The FC 203 had a switching valve on the collection gantry that diverted the flow into a vial during collection but which otherwise allowed the flow to be re-cycled or dumped to a waste receiver as required. The dispenser was fitted with a large volume 5 ml syringe. The PTFE tubing that connected the syringe to the injection needle was replaced with a coil of 1/16 in. tubing that had a capacity greater than that of the syringe such that the sample did not enter and contaminate the syringe. The collection program followed the usual procedure of ensuring that the sample lines were cleaned with fresh solvent before the calculated volume of sample solution was taken up into the holding coil. The autosampler then loaded the injection loop, injected the first sample and started the timing. At the programmed interval, the autosampler sent a signal to the fraction collector, which then commenced its cycle. Meanwhile the dispenser reloaded the injection loop with a fresh aliquot of solution and at the specified time injected the second sample. This cycle was repeated for the specified number of injections. The fractionation produced sample weights in the order of 5–30 mg. The whole process was repeated with a second batch of collection vials where a larger amount of fraction was required. Each fraction was analysed separately for copolymer chemical composition and molecular weight.

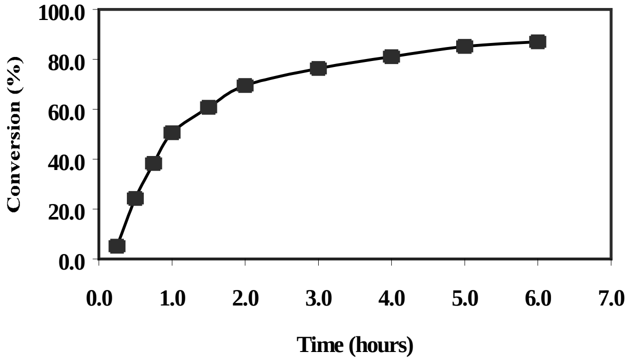

Fig. 1. The effect of time on the conversion of monomer to polymer during the batch copolymerisation of MMA and TPGDA.

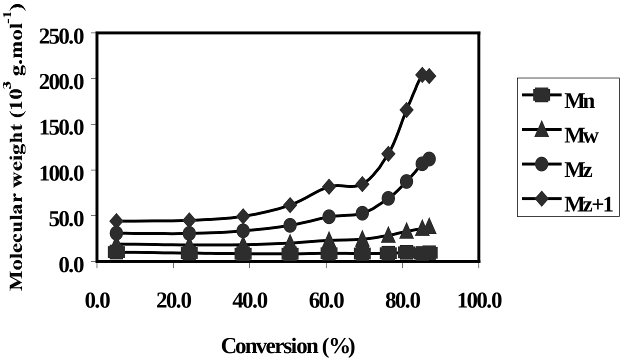

Fig. 2. The variation of molecular weight averages for poly(MMA-*co*-TPGDA) isolated at various conversions. The molecular weights were obtained from single detector GPC calibrated with linear PMMA standards.

3. Results and discussion

3.1. Polymer composition as a function of monomer conversion

Fig. 1 shows the relationship between monomer conversion and polymerisation time for the copolymerisation of MMA with TPGDA using DDM as chain transfer agent. This demonstrates that the polymer yield increases with time and reaches a plateau at approximately 90% conversion after 6 h. The compositional data derived from the NMR spectra given in Table 1 demonstrate that the diacrylate is incorporated throughout the polymerisation at a similar level to the feed composition (5.0% (w/w) diacrylate based on MMA monomer), independent of conversion. The various molecular weight averages obtained from polymers isolated at different conversions via conventional GPC are illustrated in Fig. 2. This shows that M_n (from conventional GPC) remains fairly constant throughout the polymerisation whereas M_w, M_z and $M_z + 1$ all increase with conversion, with this increase being in the order $M_z + 1 > M_z > M_w$. Since $M_z + 1/M_z > M_z/M_w > M_w/M_n$, the molecular weight distribution broadens with conversion and contains an ever increasing high molecular weight tail.

Table 1
Chemical composition and T_g of branched poly(MMA-*co*-TPGDA) copolymers obtained at different monomer conversions (0.15 mol MMA and 2.50×10^{-3} mol TPGDA were dissolved in 0.33 mol of toluene, using 1.48×10^{-3} mol DDM as chain transfer agent. The polymerisation was initiated using 9.15×10^{-4} mol of AIBN)

Time (h)	Conversion[a] (%)	[TPGDA[b]] (wt%)	T_g (°C)
0.5	24.2	5.2	96.8
1.0	50.6	5.5	77.4
2.0	69.5	5.0	80.6
4.0	81.1	5.3	96.9
6.0	87.0	5.4	95.9

[a] Evaluated from single detector GPC using an infra-red detector by comparing peak areas for polymer and residual MMA.

[b] Determined by ^{1}H NMR spectroscopy.

Fig. 3 shows the chromatograms from the TDGPC for copolymers isolated at different monomer conversions. These indicate that as the polymerisation time increases, the copolymer becomes broader in its molecular weight distribution. The chromatograms also become more non-uniform as the polymerisation time increases and this is discussed in more detail later. Unlike the chromatograms from conventional GPC, the low molecular weight tails (and M_n) in Fig. 3 do not appear to be constant. However, in TDGPC the light scattering detector response depends on molecular weight and this can cause problems in precision and accuracy at low molecular weights. Therefore, we believe that the M_n values from TDGPC in this work are potentially unreliable resulting from changes to instrument sensitivity. Interestingly, these chromatograms display similar characteristics to those obtained from hyperbranched polyesters [15]. Fig. 4 compares the molecular weights obtained from TDGPC to the molecular weights from the conventional single detector GPC experiments. At low molecular weights, the values given by the two techniques are similar but as molecular weight increases

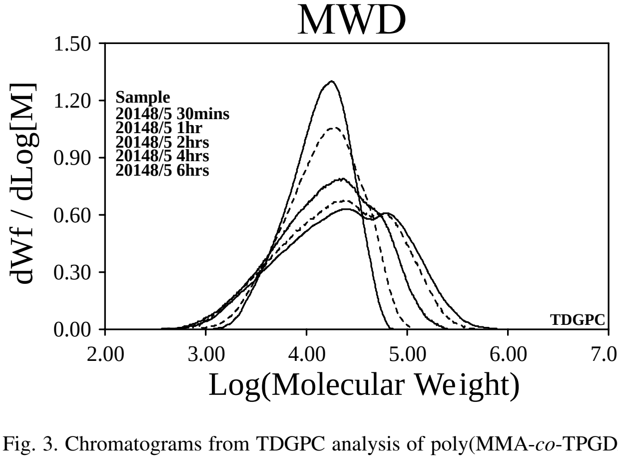

Fig. 3. Chromatograms from TDGPC analysis of poly(MMA-*co*-TPGDA) isolated at different conversions. Solid lines represent a polymerisation time of 30 mins, 2 hrs and 6 hrs whereas dashed lines represent 1 hr and 4 hrs. The figure illustrates the increase in molecular weight and broadening of molecular weight distribution with conversion.

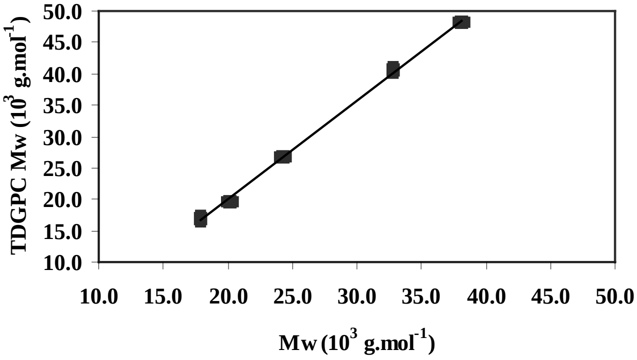

Fig. 4. Comparison of poly(MMA-*co*-TPGDA) molecular weights obtained from single detector GPC to molecular weights obtained from TDGPC, both calibrated with linear PMMA standards.

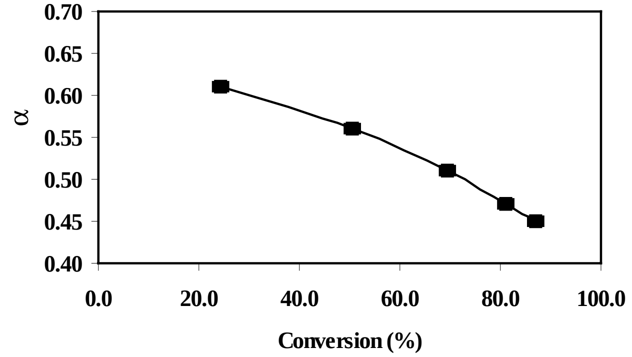

Fig. 5. The variation of the average Mark–Houwink exponent α of poly(MMA-*co*-TPGDA) isolated at various conversions.

with conversion, the M_w derived from TDGPC increases more rapidly. In TDGPC, the separation process itself is not used for any part of the calculations but merely acts as a gate-keeper for the detection system. Simplistically, the viscometer measures molecular size and the light scattering photometer measures molecular weight. The concentration term is a necessary requirement of the other two detection parameters. The data reduction step is complex but essentially the relationship between molecular size and molecular weight is established for the linear polymer control. The corresponding data from the branched polymer is then compared to that of the linear precursor. The branching information is extracted using equations that have been developed from basic geometry and fundamental polymer solution theory. The most basic information is derived from the relationship between intrinsic viscosity and molecular weight

$$\eta = KM^{\alpha}$$

This is often referred to as the Mark–Houwink relationship [24]. The exponent α has characteristic values and is typically in the region of 0.7 for linear homopolymers in a good solvent with a random coil conformation. The increase of molecular size with molecular weight is not as rapid in branched polymers as in linear polymers. This has the effect of lowering the slope of the Mark–Houwink plot giving smaller values of α. The Zimm branching factor (g') is another way of expressing the 'degree' to which a molecule has deviated from the linear model. It is the ratio of the radius of gyration (of the flexible coil) of the branched molecule to that of the linear molecule of the same molecular weight. Experimentally, g' is computed from the intrinsic viscosity ratio at constant molecular weight. There are limitations to this approximation but they do not significantly alter the interpretation of results. These branching parameters can be expressed as the averaged value over the molecular weight distribution or in graphical form as a continuously variable parameter. Fig. 5 demonstrates that the average Mark–Houwink constant α for the isolated copolymers decreases systematically with conversion and is consistent with the formation of a more compact structure arising from an increase in branching. The corresponding changes in the overall Mark–Houwink relationship for samples isolated at different conversions are shown in Fig. 6. Although not particularly obvious from the figure, the relationships are not linear and the slopes tend to decrease as a function of molecular weight within the molecular weight distribution. This suggests that the degree of branching increases with molecular weight. Table 1 demonstrates that T_g increases with conversion (as molecular weight rises) but these T_gs are much lower than those obtained from linear PMMAs of similar molecular weight. These lower T_gs are a likely result of the branched nature of the copolymers produced with the larger number of end groups likely to increase free-volume. Simultaneously, the end-to-end distances of the branched copolymers are lower than linear polymers of equivalent molecular weight and this will also have an influence. Again, this data correlates well to the situation with hyperbranched condensation polymers where T_gs tend to be much lower than linear analogues

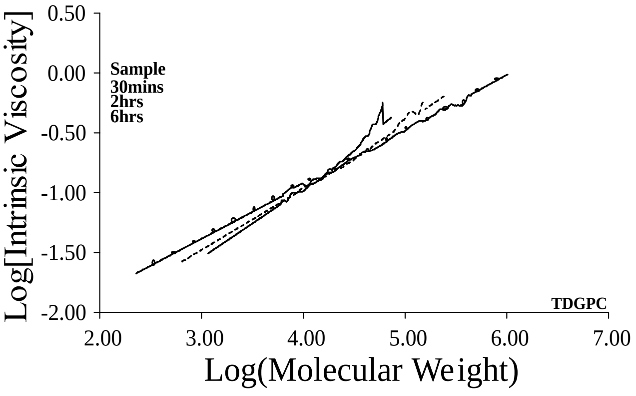

Fig. 6. The relationship between intrinsic viscosity and molecular weight illustrating the variation in the Mark–Houwink constant α across the molecular weight distribution for poly(MMA-*co*-TPGDA) isolated at different conversions. Solid lines represent a polymerisation time of 30 mins and 6 hours, whereas the dashed line represents a polymerisation time of 2 hours. The figure illustrates that the slope (and hence α) decreases with conversion.

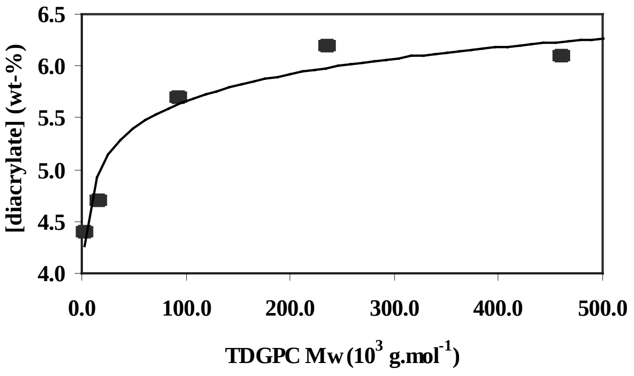

Fig. 7. The variation of TPGDA comonomer content with M_w for samples prepared by fractionating poly(MMA-*co*-TPGDA) isolated at high conversion.

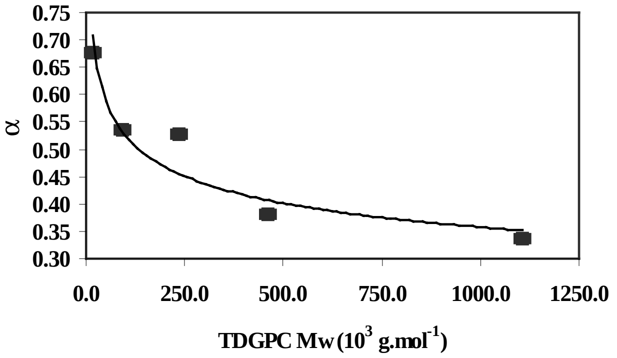

Fig. 9. The variation of the Mark–Houwink constant α with M_w for samples prepared by fractionating poly(MMA-*co*-TPGDA) isolated at high conversion.

with the nature of the high end group concentration having a strong influence [4,15–17].

3.2. Fractionation of copolymer obtained at high conversion

The polymerisation taken to 90% conversion was scaled up and the isolated copolymer was fractionated using GPC to yield a series of narrow molecular weight distribution samples with $M_w/M_n < 1.2$. Therefore, each of these fractions represents part of the original molecular weight distribution. Each fraction was then re-analysed for chemical composition (by NMR) and molecular architecture (by TDGPC). The variation of chemical composition as a function of the molecular weight of these copolymer fractions is shown in Fig. 7. Intriguingly, the data show that the amount of diacrylate incorporated increases systematically with molecular weight within the original full molecular weight distribution obtained at high conversion. Fig. 8 shows the same data in terms of the number of diacrylate units incorporated per copolymer chain. Since the diacrylate units are the source of branching, then this data confirms that the number of branches increases as molecular weight increases within the original full molecular weight distribution. The change in the Mark–Houwink constant α as a function of molecular weight for the same copolymer fractions is shown in Fig. 9. For linear PMMA this value is 0.72 and clearly for the copolymer fractions, α decreases systematically as the molecular weight increases. This is consistent with the increasing concentration of diacrylate monomer copolymerised, which would be expected to be the source of branching. A similar relationship between the geometric parameter g' and molecular weight of the copolymer fractions is shown in Fig. 10. For linear PMMA, g' is 1.0 and clearly g' falls progressively with the M_w of the copolymer fractions as the complexity of branching increases. These data support the view that copolymer with low molecular weight ($\ll$10,000 g mol^{-1}) contains a low level of branching and is likely to contain linear polymer. This results from the statistical distribution of species that will be present.

It is interesting to compare the data for the fractionated samples with the average data for the same non-fractionated copolymer. The average Mark–Houwink exponent α for the sample made at 90% conversion of monomer is 0.45. However, fractionation into samples of varying molecular weight actually demonstrates that there is a distribution in α values varying from 0.72 for the very low molecular weight fraction to 0.33 for the very high molecular weight fraction.

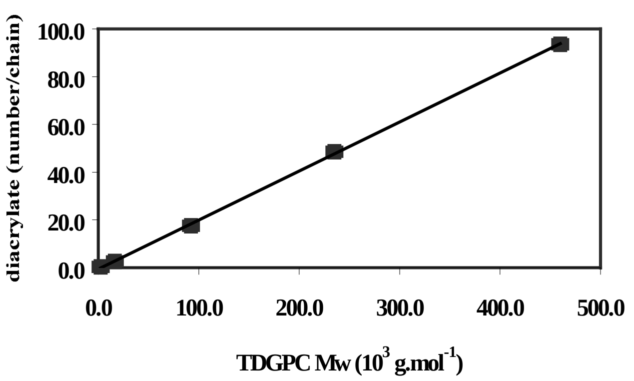

Fig. 8. The variation of the number of diacrylate units per chain with M_w for samples prepared by fractionating poly(MMA-*co*-TPGDA) isolated at high conversion.

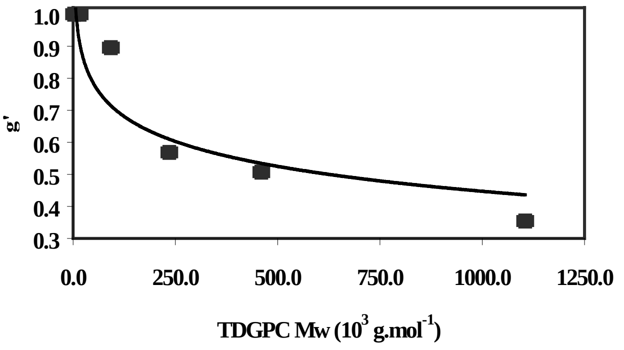

Fig. 10. The variation of the geometric parameter g' with M_w for samples prepared by fractionating poly(MMA-*co*-TPGDA) isolated at high conversion.

Table 2
The effect of CoBF concentration on the molecular weight of soluble poly(MMA-*co*-TPGDA) copolymers, characterised by single detector GPC (0.15 mol MMA and 7.50×10^{-4} mol TPGDA were dissolved in 0.33 mol of toluene. CoBF was added at various concentrations, based on the MMA concentration. The polymerisation was initiated using 9.15×10^{-4} mol of AIBN)

[CoBF] (ppm)	M_n (10^3 g mol^{-1})	M_w (10^3 g mol^{-1})	M_z (10^3 g.mol^{-1})	$M_z + 1$ (10^3 g mol^{-1})	Mw/Mn
2.5	26.9	101.8	297.4	559.6	3.7
5.0	21.2	82.9	247.0	511.7	3.9
10.0	23.9	78.7	195.1	354.9	3.3

Overall, these data compare well with data for hyperbranched polymers where average α values tend to vary from 0.6 to 0.2 depending on the degree of branching. To our knowledge, there is little information published on the chemical or physical architecture composition distribution of hyperbranched polymers. Studies on the fractionation of hyperbranched polyesters made by a one-stage polymerisation will soon be published and will show a similar reduction in α relative to linear polymer as a function of molecular weight [25], as reported here for the branched acrylic polymers. As the data shown in this report demonstrate, fractionation of branched polymers isolated at high conversion followed by analysis of the fractions is an extremely powerful method for determining both the chemical and physical architecture composition distribution as a function of molecular weight. Indeed, this is recommended as a key method for characterising branched polymers, since many branched polymers are likely to contain structural heterogeneity.

3.3. Changing the mechanism of chain transfer

The formation of branched acrylic structures from a facile, one-pot polymerisation taken to high conversion has been proven. This has been achieved by using a combination of multifunctional comonomer and mercaptan chain transfer agent. However, in the polymerisation of methacrylate monomers, CCT agents can also be used to regulate molecular weight. These are usually low spin transition metal complexes and a typical CCT agent is bis(borondifluorodimethylglyoximate) cobaltate (II) (CoBF). CoBF has the advantage that much lower quantities are required for effective reduction in polymer molecular weights [26]. Copolymerisations of MMA and TPGDA were performed using CoBF as the chain transfer agent instead of DDM. As when using DDM, soluble products were prepared by batch solution polymerisation taken to high conversion. The data in Table 2 show the average molecular weights of copolymers (determined by conventional GPC) obtained from using different concentrations of CoBF in the polymerisation. Whilst the M_n is variable, the data demonstrates that M_w increases as the concentration of CCT agent decreases. As before, NMR spectroscopy demonstrates that the amount of diacrylate incorporated is similar to the feed concentration. The copolymers are also characterised by a high concentration of vinyl groups which is consistent with the mechanism of polymerisation of MMA using CCT, where high levels of vinyl ends are formed as a result of β-hydrogen abstraction as the Co(11) is converted to Co(111) [26].

3.4. Mechanism of polymerisation

From this and other studies to be reported, it is known that

- the overall concentration of bifunctional monomer incorporated into the copolymer is similar to the feed;
- increasing the level of bifunctional monomer results in a more highly branched architecture [27];
- for a given branched copolymer, the degree of branching increases with molecular weight within the molecular weight distribution, with the lowest molecular weight containing a small amount of branching and contaminated with linear polymer;
- increasing the bifunctional monomer concentration leads to an increase in molecular weight and a higher polydispersity [27];
- the level of CTA affects molecular weight but has little effect on the level of branching.

Based on the general mechanism of free-radical polymerisation [28] and the results summarised above, the following mechanism is proposed. Primary radicals are formed via initiator decomposition and these initiate polymerisation in the conventional way. Chain propagation occurs via copolymerisation of the MMA and TPGDA. After chain transfer takes place, a ‘dormant’ polymer is produced which contains several pendant acrylate groups resulting from copolymerisation of TGPDA units. Fig. 11(a) illustrates the formation of polymer X schematically. The chain transfer agent residue then reinitiates the polymerisation. This agrees with the observation that linear polymer and lightly branched copolymer are generated at low conversion. Polymer X is dormant, since NMR spectroscopy demonstrates that pendant acrylate functional groups are present on the polymer ($\delta = 5.8$ and 6.4 ppm) which can participate in polymerisation at a later stage. The number of pendant acrylate groups is small and decreases to very low levels as the polymerisation proceeds to high conversion. Free-radicals continue to be generated throughout the course of the polymerisation, both from initiator decomposition

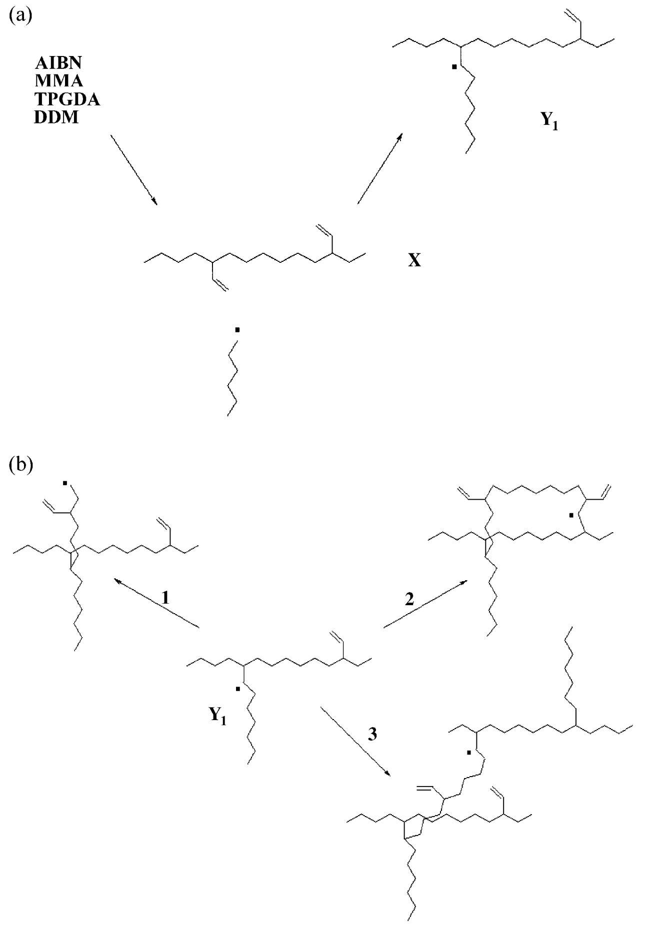

Fig. 11. (a) Proposed mechanism for chain growth:reaction of dormant chains *X*. (b) Proposed mechanism for chain growth: reaction of propagating chains Y_1 according to reactions 1, 2 and 3 (see text for details).

and chain transfer reactions. Statistically, these species will react with monomer, especially in the earlier stages of the reaction, to generate propagating radicals that grow through the pendant acrylate groups of structure X. These reactions produce propagating species such as Y_1 in Fig. 11(a). It is possible for Y_1 to react in several ways, as illustrated in Fig. 11(b):

1. propagate further monomer to form a pendant chain;
2. propagate with further monomer linking two pendant acrylate groups within the same molecule in an intramolecular fashion to form a cyclic chain;
3. propagate with further monomer linking two pendant acrylate groups within different molecules in an intermolecular fashion.

After these propagation steps, chain transfer occurs to form branched polymers. These are also dormant and contain a number of pendant acrylate groups that can participate in the polymerisation at a later stage. As polymerisation continues, propagating radicals derived from initiator or chain transfer agent will react with monomer to generate further propagating radicals that grow through the pendant acrylate groups of the dormant branched polymers, according to reactions 1, 2 and 3 above. The formation of dormant branched structures, followed by propagating chains growing through pendant acrylate groups will be repeated a number of times through the course of the polymerisation. Ultimately, a distribution of branched polymer architectures (Z) will be produced, controlled by the statistical nature of the polymerisation. In the absence of sufficient CTA, a crosslinked network of infinite molecular weight would result. In the presence of a sufficient concentration of CTA, the formation of a macroscopic network will be inhibited and indeed appropriate levels of CTA restrict the formation of microgels by limiting the structures formed to those containing branches and cycles.

For the copolymerisation of a methacrylate (M_1) with an acrylate (M_2), the corresponding reactivity ratios are typically $r_1 \sim 2.0$ and $r_2 \sim 0.5$ [29]. This means that the instantaneous copolymer composition formed at low conversion will be methacrylate rich, whereas the instantaneous copolymer composition formed at high conversion will be acrylate rich. Therefore, an increasing concentration of multifunctional monomer (and branching) will be incorporated later in the polymerisation. This agrees with the data generated from analysis of the fractionated samples. The chain transfer constants for propagating methacrylate and propagating acrylate radicals with mercaptans are quite different; for the former C_s is typically 0.6 but for the latter C_s is typically 1.7 [30]. This has the likely consequence that towards the end of the polymerisation, when much of the CTA has already been utilised and the number of propagating acrylate radicals increases, the system will be relatively starved of CTA and an increase in termination by combination (which predominates for acrylates [31]) occurs.

The fact that M_n is relatively unchanged with conversion and that low molecular weight material is linear or lightly branched, both result from the formation of new chains throughout the polymerisation (from initiator and chain transfer agent). These short chains are likely to contain little diacrylate (on average 1–2 diacrylate units for every 100 MMA units). The increase in the weight average and higher molecular weights is consistent with a number of facts. These include the proposed formation of dormant polymer chains which grow by reacting later in the polymerisation; the increasing level of bifunctional monomer incorporated due to reactivity ratios, and the likely increase in termination via combination of polymer chains containing propagating acrylate functional groups. This is quite unlike the situation in the conventional free-radical homopolymerisation of MMA to form linear polymer, typical data for which is shown in Fig. 12. This shows the variation of apparent molecular weights (from conventional GPC) with conversion during the solution polymerisation of MMA in the presence of monofunctional chain transfer agent but in the absence of bifunctional monomer. The polymerisation conditions for preparation of the linear PMMA were

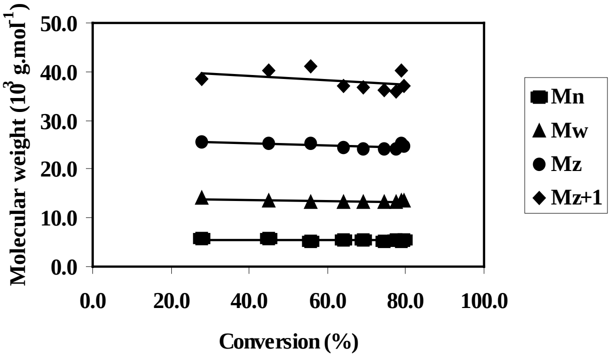

Fig. 12. The variation of molecular weight averages for PMMA homopolymer isolated at various conversions. The molecular weights were obtained from single detector GPC calibrated with linear PMMA standards.

identical to those used for synthesising the branched poly(MMA-*co*-TPGDA) polymers discussed previously (cf. Fig. 2), except that the MFM was omitted. For the homopolymerisation of MMA, the change in the average molecular weights with conversion is very different to those illustrated earlier in Fig. 2 for the copolymerisation of MMA with TPGDA. Compared to the latter, the homopolymerisation results in molecular weights that change relatively little as a function of conversion.

4. Conclusions

Branched copolymers have been synthesised by copolymerising MMA with a diacrylate monomer using a mercaptan chain transfer agent to prevent crosslinking. The apparent M_n of the copolymers remains constant whereas M_w, M_z and $M_z + 1$ increase with conversion. The copolymer chemical composition also remains essentially constant but the Mark–Houwink constant α reduces with conversion, resulting from an increase in the degree of branching. Copolymer T_g tends to increase but is always much lower than linear homopolymers of similar molecular weight.

Fractionating branched copolymer made at high conversion reveals interesting detailed information on the chemical and physical architecture composition as a function of molecular weight across the whole of the original molecular weight distribution. As molecular weight increases, the amount of diacrylate incorporated systematically rises. Simultaneously, there is an increasing discrepancy between molecular weights determined from TDGPC compared to conventional GPC. This arises from a systematic decrease in α and g' resulting from a more compact architecture with an increased number of branches.

Similar branched structures can be obtained by copolymerising MMA and diacrylate monomer using a CCT agent to prevent crosslinking. In a similar fashion to the polymerisation of MMA in the absence of multifunctional monomer, a much lower concentration of CCT agent is required to prevent crosslinking compared to mercaptans. The branched copolymer contains a relatively high concentration of vinyl end groups in the same way as PMMA homopolymers prepared by this method.

The observations are consistent with a mechanism whereby initially one end of the diacrylate is copolymerised with MMA to give linear copolymer containing pendant acrylate groups. Each remaining acrylate can then react with propagating radicals later in the polymerisation to form a branch or a loop. As conversion proceeds it is possible for branched molecules containing unreacted acrylate to couple, either via copolymerisation or by termination (since the dominant mode for termination for propagating acrylates is combination). This will lead to higher molecular weight and broadening of polydispersity. Additionally, the mismatch in reactivity ratios will cause the diacrylate to be consumed later in the polymerisation with higher molecular weight branched polymer being formed at higher conversions.

It is also worth emphasising that the approach of fractionating the branched copolymer obtained at high conversion followed by a detailed analysis of the fractions has proved to be invaluable in defining more precisely the formation of branched copolymer. More studies using this approach are required to improve our understanding of branching in polymerisations. Further studies on varying the structure and concentrations of the monofunctional monomer, multifunctional monomer, the chain transfer agent and their influence on polymer properties will be reported in the near future.

Acknowledgements

We would like to thank Mike Chisholm (Ineos Acrylics) for several useful discussions and we are grateful to Alan Bunn (ICI Technology) for NMR analysis.

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