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Facile, versatile and cost effective route to branched vinyl polymers

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Abstract

Free radical one-step polymerisation of methyl methacrylate in the presence of a crosslinking comonomer *and* balancing levels of a chain transfer agent allow facile high conversion synthesis of polymers with a branched architecture. Broad GPC curves have been obtained for these materials and branching has been demonstrated using GPC coupled with a triple detection system allowing evaluation of g', the Zimm branching factor. In addition the bridging residues in branched polymers arising from use of an unsaturated crosslinking comonomer have been chemically cleaved to yield the linear oligomers of much narrower molecular weight distribution that comprise the branched structure. The methodology promises to be generic, utilises only readily available starting materials and holds out good prospects for providing branched vinyl polymers on a technically useful scale at low cost. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Branched architecture; Chain transfer; Crosslinking

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1. Introduction

Though, in principle, polymers may be formed with many molecular architectures, in practice most synthetic macromolecules exploited technologically are either linear species or crosslinked networks [1]. Although other architectures are accessible by careful synthesis, usually the chemistry involved does not allow for convenient and low cost scale-up. Perhaps not surprisingly, therefore, although there is now a large literature on dendrimers [2–4] and hyperbranched polymers [2–5], these focus on synthetic methods and molecular structural characterisation. In addition, those reviews which do deal with solution [6] and bulk properties [7] are strong on theoretical treatments, but are rather lacking on experimental data, since large quantities of appropriate materials for study are simply not available. Progress in the case of step-growth polymers has been good and it seems likely that materials with novel and potentially useful properties could emerge [8,9], although larger scale syntheses are still required to develop further our knowledge in this area [10,11]. In the case of vinyl polymers as well there is considerable technological interest in novel architectures and recently some ingenious methodology has emerged [12,13]. Fréchet and his co-workers have also reported on a self-condensing vinyl polymerisation (SCVP) to produce hyperbranched polymers, using "living cationic" [14], "group transfer" [15] and "living free-radical" processes [16,17]. Useful as the SCVP approach is, it does involve vinyl monomers which are additionally functionalised to allow "self-condensation" to occur. Likewise, the approach by Muller and co-workers in producing hyperbranched polymers by group transfer polymerisation [18], and the strategy by Matyjasewski et al. employing atom transfer radical polymerisation (ATRP) [19,20], though very elegant, cannot be applied generally and require the use of specialised monomers. Indeed to our knowledge no facile and broadly applicable method for transforming simple routine vinyl monomers to branched polymers has been reported to date.

In free-radical polymerisation, the inclusion of only small amounts (fractions of a percent) of bifunctional monomer (crosslinker) usually 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 [21], and more recently by Antonietti and Rosenauer [22], studying the styrene/divinylbenzene system has mapped out the interface between networks (macrogel) and microgel. Indeed implicit in these works [21,22] and others [23] is the idea that branched polymers are precursors to crosslinked gels. Having said this, irrespective of how the

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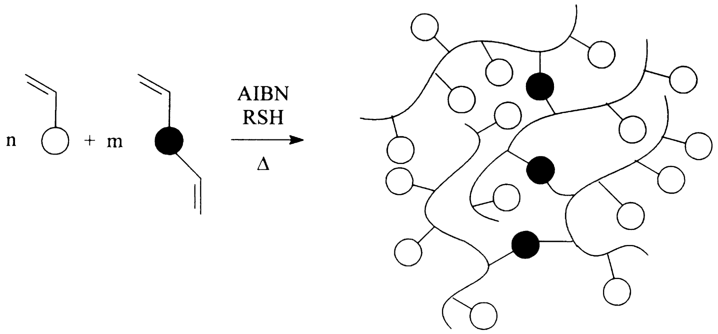

Fig. 1. Synthesis of branched vinyl polymer using a balance of crosslinker and radical transfer agent.

conditions of polymerisations are manipulated, it is very difficult to imagine that high dilution copolymerisations of a bifunctional and monofunctional comonomer could form the basis of a technology for producing large and exploitable quantities of branched spieces. In complete contract, however, we now report our initial findings on how the simple expedient of including a suitable free radical transfer agent opens up the prospect of providing a practical and highly convenient synthesis of branched vinyl polymers.

2. Results and discussion

The basic concept we have now developed is to carry out a conventional free radical solution vinyl polymerisation (at ~40 vol.% comonomers) in the presence of a crosslinker, but to avoid network formation by balancing the level of crosslinker employed with an appropriate level of chain transfer agent (Fig. 1). In our initial proof of concept we have polymerised methyl methacrylate (MMA) with but-2-ene-1,4-diacrylate (BDA) using 1-dodecanethiol (DDT) as the transfer agent. By employing BDA as the brancher–crosslinker we planned to cleave any branched polymers via ozonolysis of the internal double bond in each BDA residue, degrading the branched system to the lower molecular weight linear components comprising the branched structure.

Table 1
Co-polymerisation of MMA and BDA in the presence of DDT (see Section 3)

Polymer	BDA (mol%)	DDT (mol%)	Polymer yield(%)	Gel formation
1	2	0	~100	Yes
2	1	0	~100	Yes
3	10	1	~100	Yes
4	10	3	~100	Yes
5	10	10	67	Yes
6	1	1	89	No
7	0.5	1	97	No
8	1	0.5	~100	Yes
9	2	2	77	No

Copolymerisations of MMA and BDA were carried out in toluene solution under vacuum at 80°C using a standard methodology. Table 1 summarises the results obtained. For those reactions with >1 mol% crosslinker and no thiol the reactions gelled. This is as expected and in particular concurs with the results of Degoulet et al. [24] who reported the attempted synthesis of branched PMMA by polymerising MMA with a low level (1 mol%) of ethyleneglycol dimethacrylate, but could only isolate useful material up to ~20% conversion, beyond which the system gelled ($\bar{M}_w$ reported to be $> 15 \times 10^6$). Likewise Kratochvil et al. utilised similar levels of crosslinker and had to restrict conversions generally to less than 10% to produce soluble product [25]. In our hands those systems with a high level of crosslinker (~10 mol%) and varying levels of transfer agent (1–10 mol%) also gelled. However, in reactions 6, 7 and 9 (Table 1) the polymeric product was fully soluble and in each case the reaction solution was isotropic to the eye before isolation of the polymer. In these three examples the BDA crosslinker was employed at a relatively low level (≤ 2 mol%) and the chain transfer agent was present either at the same or a higher level than BDA. With 6, 7 and 9 the isolated (non-optimised) yield of soluble polymer was high (77–97%). ^{13}C (68 MHz, $CDCl_3$) solution-phase NMR spectra confirmed the presence of BDA residues in the macromolecular products with the –CH=CH– resonances clearly visible in the region 120–140 ppm.

Ozonides of polymers 6,7 and 9 were prepared by a standard procedure [26] and then decomposed using KI/acetic acid. ^{13}C (68 MHz, $CDCl_3$) solution phase NMR spectra of the recovered products showed complete loss of resonances at 120–140 ppm confirming scission of internal double bonds in the branching BDA residues.

Gel permeation chromatographic analysis (GPC) of the polymers 6,7 and 9, and the three products of their ozonolysis yielded the chromatograms shown in Fig. 2. The computed data shown in Table 2 represent polystyrene equivalent molecular weights, and the computation is non-sophisticated making no allowance for architecture. Clearly, however, the very complex and broad molecular weight distributions of 6, 7 and 9 are sharpened considerably in their ozonolysis products which display typical rather

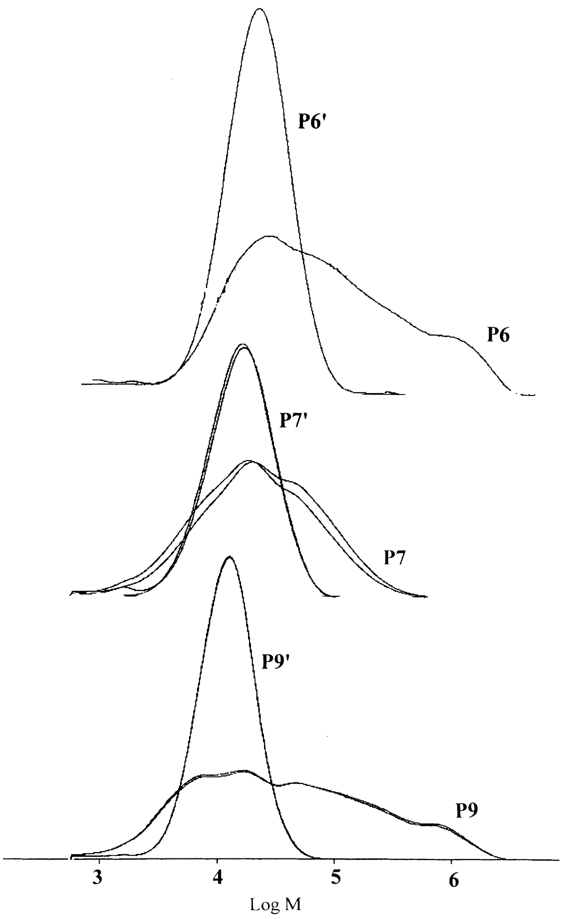

Fig. 2. Gel permeation chromatograms of polymer samples 6, 7 and 9, and their corresponding ozonised products 6′, 7′ and 9′.

symmetric Guassian-type distributions. At this stage the raw chromatograms of 6, 7 and 9 are perhaps more important than the computed data. In the case of 6 and 9, it is tempting to say that the products have (at least) three components. The first is a low molecular weight species, which seems to correspond to the ozonolysis product and may well, therefore, be a linear fraction. The second with $\log M \sim 5$ is most likely a branched species and the third with $\log M \sim 6$ is either more extensively branched or could even be a microgel fraction. Interestingly polymer 7 seems to be devoid of the fraction at $\log M \sim 6$, and since this species was produced with a crosslinker/transfer agent mole ratio only half that used with 6 and 9, the higher level of transfer agent would be expected to minimise potential microgelation. However, this interpretation must be regarded as tentative. Despite their apparent complexity, the multimodal appearance of these chromatograms is similar to that shown by a number of hyperbranched polymers recently reported [14,27–29]. The reason for and interpretation of the multimodality in the present system, and indeed in the others reported in the literature, is the basis of further work in our own laboratory, and is also being addressed by other research groups.

Table 2
GPC molecular weight data (duplicate analyses) for BDA branched PMMA samples produced in solution

Sample	Original polymer			Polymer after ozonolysis		
	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n
6	222,000	17,300	12.8	23,600	12,100	2.0
	213,000	17,400	12.2	23,900	12,100	2.0
7	38,900	9,090	4.3	18,500	11,200	1.7
	45,200	10,700	4.2	18,500	9,550	1.9
9	150,000	10,600	14.1	13,800	9,590	1.4
	157,000	10,900	14.4	13,700	9,550	1.4

Further characterisation of the branched polymer products was performed using triple detector GPC in the case of additional samples where tripropylene glycol diacrylate (TPGDA) was the chosen difunctional monomer and again DDT was the chain transfer agent. Once again, solution polymerisations of MMA were taken to high conversion with the product being fully soluble, with no gelation apparent.

With these samples GPC analysis was performed on chloroform solutions using a triple detector (TD-GPC) and the acquired data manipulated with Trisec Version 3 software (Viscotek). This yielded values for $\bar{M}_w$, $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, g' and α (where g' is the Zimm branching factor [30], and α the Mark–Houwink parameter [31]. The data in Table 3 are derived from both conventional GPC and TD-GPC analysis of the TPGDA-based polymers. Control linear PMMA homopolymers produced Mark–Houwink α values of 0.7 and the ratio of the radius of gyration of branched species to that of a linear species of the same molecular weight $g' = 1$. Both of these values indicate the absence of branching. For sample 1 in Table 3 prepared using 1.5% TPGDA both g' and α are significantly reduced to 0.59 and 0.56, respectively, indicating non-linear architecture. Both parameters are further reduced to 0.54 and 0.50, respectively, in the case of sample 2 when the TPGDA concentration is increased to 3%. It is clear, therefore, that the level of branching increases with TPGDA concentration. Additionally, the molecular weights ($\bar{M}_w$) increase and broader molecular weight distributions are produced. The molecular weights from conventional GPC are lower than those from TD-GPC, since the former samples are analysed via a single detector using linear standards for calibration. Conventional GPC does not take account of the different molecular size-molecular weight relationships for branched and linear polymers. Discrepancies between molecular weights from conventional and TD-GPC become greater as the molecular weight increases and more details of this will be reported in due course.

It is quite clear, therefore, that the strategy of balancing the level of a crosslinking comonomer with that of a free radical chain transfer agent in order to generate substantially branched vinyl polymers is viable. Such polymerisations

Table 3
Molecular weight, branching data and Mark–Houwink parameter for TPGDA branched PMMA

Sample	Method of analysis	DDT (wt%)	TPGDA (wt%)	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	g'	α
10	GPC	2.0	1.5	18,029	6745	2.67	–	–
	TD-GPC	2.0	1.5	21,850	11,750	1.86	0.59	0.56
11	GPC	2.0	3.0	27,330	8380	3.16	–	–
	TD-GPC	2.0	3.0	32,800	13,800	2.36	0.54	0.50

can be taken *to high conversion* while avoiding gelation, and we anticipate that the products obtained will be eminently processable. The approach holds out good prospects of being generic and utilises only routine reactants readily available in bulk at low cost.

Currently we are examining the scope of this strategy with methacrylate and other monomer systems, characterising fractionated samples to get more detailed molecular structural information on the branched products, and probing the bulk physical properties of these materials.

3. Experimental

3.1. Solution polymerisation procedure

Using sample 6 as an example distilled MMA (5.8 ml, 5.7 g, 5.7×10^{-2} mol), BDA (0.11 g, 5.7×10^{-4} mol), DDT (0.115 g, 5.7×10^{-4} mol) and AIBN (0.10 g, 5.7×10^{-4} mol) in dry toluene (8 ml) were introduced into a small round-bottomed flask fitted with a Young's vacuum tap. The solution was degassed by six "freeze–pump–thaw" cycles, and then heated under vacuum at 80°C for 16 h. The isotropic viscous solution formed was poured into methanol and the precipitated polymer vacuum dried (5.1 g, 89%). In the case of the PMMA samples 10 and 11 employing TPGDA as the crosslinker neither the monomers nor the toluene were dried before use and solution polymerisation was performed under N_2.

3.2. Ozonolysis procedure

Polymer 6 (1 g) in chloroform (50 ml) was chilled to −78°C (dry ice/acetone) (−20°C, ice/brine for polymers 7, 9) and then treated with O_3 for 30 min. At this point the solution was blue and excess O_3 was removed by flushing with N_2 for 10 min. On warming the solution to room temperature KI (6 g) and acetic acid (30 ml) were added and the mixture was left for 4 days. Sodium thiosulfate (50 ml, 10% aq. solution) and ethyl acetate (50 ml) were added and the mixture shaken. The organic layer was collected and aqueous layer extracted with more ethyl acetate (2 × 100 ml). The combined organic layers were dried with $MgSO_4$, the solution concentrated, and the polymer precipitated by addition to MeOH. Drying yielded a white solid (0.42 g, 42% from 6; 0.5 g, 50% from 7; 0.2 g, 20% from 9). (*Note*: the present yields (20–50%) do not reflect incomplete ozonisation and cleavage, but are a feature of the difficulty of work-up. Further optimisation of the isolation procedure is undoubtedly possible, but there is no reason to doubt that the recovered material is fully representative of the cleaved product.)

3.3. Standard GPC analysis

Columns, Polymer Laboratories 2 × mixed bed D, 30 cm, 5 μm; solvent, THF; flow-rate, 1 ml min^{-1}; temp. 30°C; detector, RI; calibration, polystyrene standards.

3.4. Triple detection GPC (TD-GPC) analysis

Viscotek system employing a laser differential refractometer, a differential viscometer and a right angle laser light scattering photometer; column, Polymer Standards Service (PSS) mixed bed; solvent, $CHCl_3$; flow rate, 1 ml min^{-1}; temp. 30°C.

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