Facile Synthesis of Branched Poly(vinyl alcohol)s

R. Baudry† and D. C. Sherrington*

Department of Pure and Applied Chemistry, Westchem Graduate School of Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, Scotland, U.K.

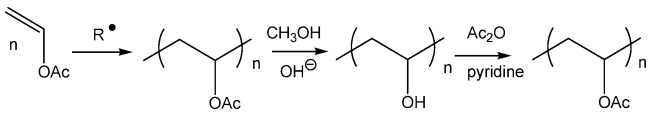
Received June 1, 2006; Revised Manuscript Received June 6, 2006

ABSTRACT: Poly(vinyl alcohol) (PVOH) is a ubiquitous synthetic polymer that finds widespread application in biological and medical products through to personal, domestic, and industrial products. The currently available range of materials all have linear backbone architectures with interesting solubility, rheological, and interfacial properties. The latter might be significantly broadened if complementary polymers with branched backbone architectures could be synthesized, especially if the methodology involved only minor changes from that currently practiced. We have now synthesized branched PVOHs via conventional free radical copolymerization of vinyl acetate (VAc) and triallyl-triazine-trione (TTT), in 2-isopropoxy ethanol (IPE) solvent in the presence of appropriate thiol free radical chain transfer agents, followed by alcoholysis of the so-formed branched poly(vinyl acetates)s (PVAc)s with methanol. Balancing the mole ratio of TTT to thiol allows high conversion to branched materials to be achieved while inhibiting cross-linking and gelation of the products. The branch points derived from the TTT comonomer have been shown to be conserved during the alcoholysis step, and extensive characterization of the PVAc precursors and the derived PVOHs using multiple detector size exclusion chromatographic (SEC) instrumentation has confirmed the highly branched nature of both groups of polymers. Final confirmation of the branched architecture of the PVOH samples has been made by reacetylation of some samples, in effect to regenerate their PVAc precursors. SEC analysis of the latter has indeed shown these to be architecturally very similar to the original precursor PVAcs. This novel methodology for synthesizing branched PVOHs involves relatively minor adjustments to the currently used industrial process for linear PVOHs and so offers good prospects for scale-up and exploitation.

Introduction

Poly(vinyl alcohol) (PVOH) has become an invaluable component of numerous personal, domestic and industrial products,[1] and more recently, it has proved attractive for exploitation in the biomedical field, not the least because of its blood compatibility.[2] Commercially sourced materials have a linear backbone architecture (see below), and aqueous solutions tend to exhibit high viscosity even at low concentrations as a result of H-bonding effects. Access to branched analogues of PVOH would be extremely attractive complementary materials to linear PVOHs for chemists, pharmaceutical chemists, bioscientists, and biotechnologists because of the different physical properties offered by such branched species, e.g., reduced solution viscosity.[3] Since the hypothetical precursor monomer, vinyl alcohol, exists predominantly as its tautomer, acetaldehyde, PVOH cannot be synthesized directly and conveniently from this precursor. In practice therefore the starting point is usually vinyl acetate (VAc) which is polymerized by conventional free radical methodology to produce poly(vinyl acetate) (PVAc), and then the latter is hydrolyzed or more usually subjected to alcoholysis using methanol to yield the corresponding PVOH[4] (Scheme 1, steps 1 and 2). Various grades of the latter each with a different molar mass and "degree of hydrolysis" are available from different manufacturers. An intrinsic feature of PVAcs produced by conventional free radical polymerization is their branched architecture. Meticulous work by Iedema et al.[5] has shown this intrinsic branching to be very low, typically ~1 branch per 1000 VAc segments, and this is likely to be the case with the "linear" reference sample of PVAc used in the present work. Though there appears to remain some uncertainty about the quantitative assignment of various mechanisms in this respect, in fact most branching is believed to arise from a free radical chain transfer reaction involving the pendant acetate methyl groups.[4] This is a key structural feature because alcoholysis of the acetate groups in converting PVAc to PVOH in effect removes the intrinsic branches in the PVAc precursor, such that commercial samples of PVOH have essentially a linear backbone architecture. Recently Rimmer et al. have reported a novel route to branched PVAcs utilizing conventional free radical polymerization of VAc with chain transfer to allylic carbonate comonomers.[6] Unfortunately the conversions reported are far from quantitative, and more importantly, in terms of these species being potential precursors to branched PVOHs, the route does not seem attractive since the branch points are carbonate esters which are likely to be cleaved during the conversion of the acetate pendent groups to hydroxyl groups. In contrast Stenzel et al.[7] have reported the successful synthesis of PVOHs with a comb-type architecture. The precursor PVAcs were produced by MADIX/RAFT polymerization techniques which offer good structural control, but unfortunately the procedure is a complex multistep process. While this offers materials that might be suitable for small-scale niche applications, is unlikely to make large quantities of branched PVOHs widely available for investigation by the broad scientific community who might benefit from access to such materials. In addition, the MADIX/RAFT derived materials contain an ester linkage at each branch point which seems to survive the acetate alcoholysis step, but which nevertheless presents a key weak link in the architecture which might cleave later in use under more forcing conditions. Indeed the earlier failed attempt by this group to produce PVOH "star" polymers did result in degradative cleavage of the

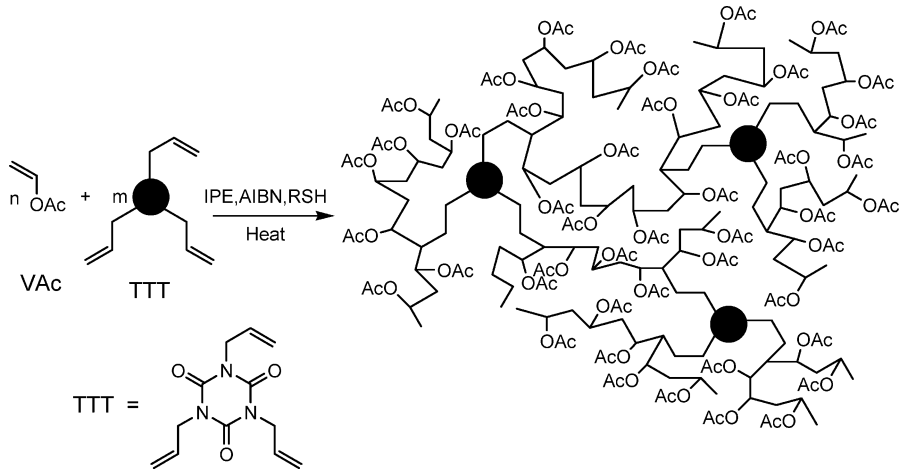
Scheme 1. Polymerization of VAc to PVAc, Methanolysis of the Latter to PVOH, and Reacetylation to PVOHAc



* Corresponding author. E-mail: d.sherrington@strath.ac.uk.
† E-mail: roselyne.baudry@strath.ac.uk.

10.1021/ma061221d CCC: $33.50
Published on Web 07/06/2006

Scheme 2. Synthesis of Branched Poly(vinyl acetate)s (*b*-PVAcs) in Isopropoxy Ethanol (IPE), via Conventional Free Radical Copolymerization of VAc and a Trifunctional Monomer,TTT, in the Presence of a Thiol (RSH) To Aid in Inhibiting Cross-Linking



precursor PVAc "stars" as a result of the labile xanthate linkage in the precursors.[7a]

Over the past few years we have developed a facile and generic strategy for synthesizing branched vinyl polymers via conventional free radical polymerization chemistry[8] that uses only low cost readily available starting materials, and we have demonstrated that a similar strategy is applicable to living polymerizations as well.[9] The approach involves the copolymerization of a monofunctional monomer with a polyfunctional comonomer (usually difunctional) under experimental conditions that inhibit cross-linking and macrogelation. With conventional free radical polymerizations this involves the use of controlled levels of an effective transfer agent such as a thiol (Scheme 2) or a catalytic chain transfer agent such as a cobalt oxime.[10] We realized some time ago that in principle this offered as a route to branched PVOHs via branched PVAc precursors but our early attempts to achieve this were thwarted by the fact that common difunctional branching comonomers either did not copolymerize readily with VAc (e.g., divinylbenzene) or when they did so, each introduced a functional group linkage in the branch which was unstable during the final acetate to hydroxyl group conversion step (e.g. di- and triacrylates). We now report on the solution to these problems and the facile synthesis of branched PVOHs using a methodology that is readily scalable and offers good prospects for making exploitable quantities of these materials available to other scientists.

Experimental Section

Materials. Vinyl acetate (VAc, 99%, Aldrich) was passed through a basic alumina column and azobis(isobutyronitrile) (AIBN, Aldrich) was recrystallized from acetone before use. 2- Isopropoxyethanol (IPE, 99%, Lancaster), 1,3,5-triallyl-1,3,5-triazine-2,4,6(*1H,3H,5H*)-trione (TTT, 98%, Acros), 2-mercaptoethanol (ME, Aldrich), 3-mercaptopropane-1,2-diol (MPD, 98%, Aldrich), di(2-mercaptoethyl)ether (DMEE, 95%, Aldrich), pyridine (Acros Organic), and acetic anhydride (98%, Aldrich) were used as received.

Polymer Syntheses. Synthesis of Branched PVAcs. Typically VAc (5 g, 58 mmol), TTT, chain transfer agent (ME, MPD, and DMEE) (see Table 1 for molar feed ratios), and AIBN (2 mol % relative to double bonds) were added sequentially to IPE (25 mL) in a 50 mL Schlenk flask. The reaction mixture was degassed in three freeze−pump−thaw cycles. The polymerization reaction was then allowed to proceed at 60 °C under nitrogen. After 24 h, another 2 mol % (relative to double bonds) of AIBN was added and the reaction continued for a further 48 h. At this stage, the conversions were determined by direct ^{1}H NMR analysis of the reaction mixture.

Table 1. Synthesis of Branched Poly(vinyl acetate)s and Poly(vinyl alcohol)s

PVAcs					PVOHs	
sample	CTA	mole ratio VAc/TTT/CTA	convn (%)	yield (%)	sample	yield (%)
b-PVAc1	ME	100/2/6	92	75[a]	*b*-PVOH1	69
b-PVAc2	ME	100/3/9	*b*	52	*b*-PVOH2	77
b-PVAc3	ME	100/3/9	93	71	*b*-PVOH3	88
b-PVAc4	ME	100/3/10	94	69	*b*-PVOH4	94
b-PVAc5	ME	100/5/17	86	61	*b*-PVOH5[c]	94
b-PVAc6	MPD	100/2/6	92	86[a]	*b*-PVOH6	64
b-PVAc7	MPD	100/3/9	90	60	*b*-PVOH7	76
b-PVAc8	MPD	100/3/9	93	75	*b*-PVOH8	87
b-PVAc9	MPD	100/3/10	93	66	*b*-PVOH9	97
b-PVAc10	MPD	100/5/17	89	56	*b*-PVOH10[c]	95
b-PVAc11	DMEE	100/2/4	89	76[a]	*b*-PVOH11	71
b-PVAc12	DMEE	100/3/6	94	70	*b*-PVOH12[c]	81
b-PVAc13	DMEE	100/3/7	89	59	*b*-PVOH13[c]	93
b-PVAc14	DMEE	100/5/12	85	62	*b*-PVOH14[c]	84

[a] One precipitation (acetone/*n*-pentane). [b] Not measured. [c] Insoluble in water.

The solution was evaporated under vacuum, and the resulting product was dissolved in the minimum volume of acetone and precipitated in *n*-pentane (300 mL). The supernatant liquid was decanted off and the polymer was dried under vacuum. It was then redissolved in the minimum volume of acetone and precipitated in distilled water (600 mL). Initially two successive precipitations were carried out to maximize the purity of the products but this was later reduced to one which improved the recovery (%). The resultant PVAc was collected by filtration and dried to constant mass under vacuum at 40 °C.

Synthesis of Branched PVOHs. Into a 50 mL three-necked round-bottomed flask equipped with a stirrer and condenser were added PVAc (0.9 g) and sodium hydroxide (5 mol % relative to theoretical content of acetate groups) and suspended in methanol (30 mL). The solution was refluxed overnight at 65 °C. After cooling, the reaction mixture was concentrated under vacuum and the addition of acetone (50 mL) allowed the precipitation of the product. The resultant PVOH was collected by filtration and dried to constant mass under vacuum at 40 °C .

Acetylation of Branched PVOH. In a typical procedure, a branched PVOH (0.25 g) was dissolved in anhydrous pyridine (20 mL). Acetic anhydride (0.8 mL) in anhydrous pyridine (10 mL) was added dropwise and the solution was refluxed for 5 h under nitrogen. After cooling, the reaction mixture was concentrated under vacuum, the residue dissolved in the minimum volume of acetone and the product precipitated in cold water (200 mL). The resultant PVAc was collected by filtration and dried to constant mass under vacuum at 40 °C .

Polymer Characterization. NMR Spectroscopy. ^{1}H NMR spectra were recorded on a 400 MHz Bruker DPX-400 spectrometer using $CDCl_3$ (for *b*-PVAcs) and d_6-DMSO (for *b*-PVOHs) as the solvent in 5 mm NMR tubes. In all of the spectra, the residual signal of the solvent was used as a reference.

FTIR Spectroscopy. FTIR spectra were recorded on a Perkin-Elmer 1600 Series instrument using a diamond compression cell for polymer samples and a KBr cell for monomers.

Molar Mass Analysis of *b*-PVAcs. Analyses were conducted either with a multiangle light scattering−size exclusion chromatograph (MALS/SEC) or with a triple detection−size exclusion chromatograph (TD−SEC). The data for the branched samples were compared with that of a linear PVAc (from Aldrich) which analyzed as follows: $M_n = 49\,000$ g/mol, $M_w = 199\,000$ g/mol, and $M_w/M_n = 4$. The MALS/SEC instrument package was supplied by Optokem and comprised the following equipment: (i) a Jones Chromatography 760 series Solvent D-Gasser, (ii) a Waters 515 HPLC pump operating at room temperature, (iii) a Jasco AS-950 autosampler with 50 position sample racks, (iv) a column oven, (v) a set of three Styragel HR 2, HR 4, and HR 6 designation 7.8 × 300 mm GPC columns, and (vi) two detectors connected in a serial configuration: a multiangle light scattering detector (mini-Dawn) supplied by Wyatt Technology and an interferometer refractomer detector (Optilab DSP) supplied by Wyatt Technology. THF was the mobile phase, the column oven temperature was set to 40 °C, and the flow rate was 1 mL/min. The samples were prepared for injection by dissolving 10 mg of polymer in 1 mL of HPLC grade THF and filtered of with an Acrodisc 0.2 μm PTFE membrane. 0.2 mL of this mixture was then injected, and data were collected for 40 min. The wavelength used was 690 nm. The d*n*/d*c* value used was 0.054. Astra for Windows was used to collect and process the detector signals and to produce the molar mass distribution curves and molar mass vs elution volume and rms radius of gyration vs molar mass plots.

The TD-SEC instrument was used to determine not only molar mass data but also the intrinsic viscosities and hence the Mark−Houwink α value of each sample. A Polymer Laboratories PL-GPC50 integrated GPC system was employed with THF (containing 2% triethylamine) as the eluent at a flow rate of 1 mL/min at 30 °C. The instrument was equipped with two 5 μm (30 cm) mixed C columns, a WellChrom K-2301 refractive index detector operating at 950 ± 30 nm, a Precision detector PD 2020 light scattering detector (at scattering angles of 90 and 15 °C), and a BV400RT viscosity detector. Molar masses of the branched polymers were determined by the triple detection method using PL Cirrus Multi online software (version 2.0) supplied by Polymer Laboratories. A series of near-monodisperse linear poly(methyl methacrylate) standards (from Polymer Labs) was used to construct the calibration curve. The d*n*/d*c* value used was 0.054.

Molar Mass Analysis of *b*-PVOHs. Analyses were performed using a MALS/SEC instrument with 20% aqueous methanol with 0.05 M $NaNO_3$ adjusted to pH 9 as the aqueous eluent at a flow rate of 1 mL per minute and a sample injection volume of 100 μL. The instrument was fitted with a Polymer Laboratories PL mixed C and mixed D column set at 40 °C. Detection was carried out using a Wyatt Dawn DSP laser photometer with a Jasco RI detector. The samples were made up at 0.5%, 25 mg per 5 mL of eluent, then filtered through a 0.45 μm filter. The d*n*/d*c* value used was 0.15. The data for the branched samples were compared with that of a broad linear PVOH 99% hydrolyzed (from Aldrich) which analyzed as follows: $M_n = 123\,000$ g/mol, $M_w = 145\,000$ g/mol and $M_w/M_n = 1.42$.

Elemental Microanalyses. These were performed as an in-house service on a Perkin-Elmer 2400 analyzer.

Results and Discussion

Synthesis and Characterization of Branched PVAcs. The branched PVAcs (*b*-PVAc1−14) were all produced with high conversion of monomer in IPE solvent as indicated by the absence of any significant resonances associated with hydrogen atoms in the vinyl groups of the comonomers in the ^{1}H NMR spectra of the final reaction mixtures. The corresponding isolated yields from double precipitations are also good but are improved by restricting the workup to a single precipitation (Table 1). The losses in the workup arise primarily from a small component that does not precipitate and we believe that this is a low molar mass material. The losses are not associated with an insoluble microgel fraction and the blocking of filters etc. Regarding the choice of the transfer agent, 2-mercaptoethanol has previously been used as such in VAc polymerizations[11] and so in the present work we opted to employ similar hydrophilic thiols (ME, MPD, and DMEE). The incorporation of these residues and the TTT branching comonomer is confirmed by the ^{1}H NMR spectra of the isolated polymers (Supporting Information) which display resonances in principle assignable to these components. Unfortunately, however, these signals are of low intensity and also overlap with less clearly identifiable signals, hence precluding the use of these in quantifying the levels of TTT and transfer agent residues present in the polymers. However, further evidence for the presence of these moieties is afforded by the corresponding elemental microanalytical data. For example incorporation of all the feed of VAc/TTT/CTA = 100/5/12 for *b*-PVAc 14 would require ∼2 wt % N and ∼7 wt % S in the product and the experimentally determined values are ∼3 wt % and ∼4 wt % respectively. Typically the N wt % is somewhat higher than expected and the S wt % lower. Since significant levels of AIBN initiator are used in the polymerizations the high N wt % is reasonable. The lower than expected S wt % is more difficult to account for especially bearing in mind the reported high chain transfer constant for butanethiol in VAc polymerizations.[12] The most unambiguous direct evidence for the efficient incorporation of the TTT branching comonomer however is afforded by the FTIR spectra of the *b*-PVAcs (see Supporting Information). Characteristically the strong ester carbonyl stretching band at ∼1726 cm^{-1} is accompanied by the equally strong carbonyl band of the TTT segments at ∼1686 cm^{-1}.

The range of polymerization reaction compositions shown in Table 1 represent the "safe" scope for producing soluble PVAc products in the presence of TTT comonomer and the use of a transfer agent such as a thiol seems essential to achieve this. Thus, for example reducing the ME content of the feed progressively in the series VAc/TTT/ME 100/3/*X* (where *X* = 8,6,4,2,1 and 0) yields a soluble product for *X* = 8 with M_w ∼ 1 200 000, but thereafter, the reaction mixtures, though apparently isotropic, in fact contain microgel. The reaction mixtures become difficult or impossible to filter during routine sample preparation for MALS/SEC analysis, and where we have risked introducing such samples into our instrument, the output from the MALS detector is anomalous at the low elution volume limit of the columns. Indeed as a result of what we believe is contamination by microgel, an artifact in the signal can be retained when subsequent linear polymer samples are analyzed. Considerable caution is therefore advised when employing MALS/SEC with samples likely to contain significant levels of microgel. Though the thiol reagent is very important in producing branched rather than cross-linked products, the contribution of the IPE solvent as a transfer agent[13] is also significant and is demonstrated in two control polymerizations employing a mole feed ratio VAc/TTT/ME = 100/3/10 with ethyl acetate and ethanol as the solvent in place of IPE. A macrogel is formed in the former solvent whereas use of the latter solvent yields microgel that could not be analyzed using our MALS/SEC instrument.

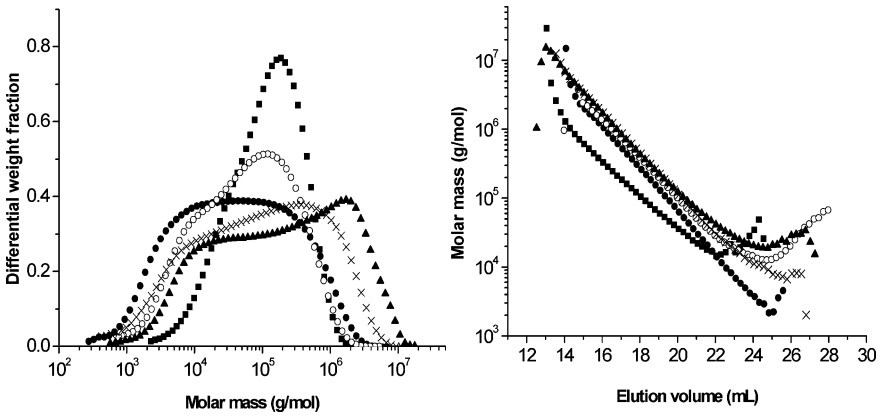


Figure 1. MALS/SEC molar mass distribution curves (left) and SEC molar mass vs elution plots (right) for (■) linear PVAc reference polymer (M_w = 199 000), (●) *b*-PVAc1, (○) *b*-PVAc2, (×) *b*-PVAc3, and (▲) *b*-PVAc4.

TTT is of course potentially a trifunctional comonomer, and assuming that all three allyl groups do participate in chain propagation, the targeted average levels of branching represented by the VAc/TTT comonomer feed mole ratios in Table 1 range from one branch every 16/17 VAc segments, to one branch every 6/7 VAc segments. In other words, the targeted levels of branching are very high and far above those arising from any intrinsic side reactions in VAc free radical polymerization. It could however be argued that the three allyl groups in TTT might act preferentially as efficient radical transfer species via abstraction of their allylic H atoms, rather than each $H_2C{=}CH-$ group participating in free radical vinyl addition reactions i.e., polymer chain propagation. If this were the case the levels of TTT used in our polymerizations would almost certainly give rise only to oligomeric products, especially bearing in mind that a high level of a thiol chain transfer agent is a component of the reaction mixtures and that the IPE solvent is also a chain transfer species.[13] It does seem therefore that the radical derived from VAc is sufficiently reactive to undergo efficient addition to the allyl groups in TTT, and interestingly Rimmer et al. have similar evidence in the case of an allylic carbonate monomer.[6] Furthermore, our identification and exploitation of TTT as a potential chain branching comonomer in VAc polymerizations was triggered by the work of Li et al.[2] who have used TTT as a very effective cross-linking comonomer in the suspension copolymerization of VAc to produce well-defined spherical macroporous PVAc beads.

The three thiol radical transfer agents chosen for investigation, ME, MPD and DMEE, were selected because of their potential hydrophilicity when incorporated into branched PVOHs. Their role is of course to inhibit any potential cross-linking by terminating the growth of each primary PVAc chain and initiating growth of a second independent chain, hence favoring the formation of branched products. Interestingly DMEE which carries two thiol groups per molecule does not appear to be more efficient in transfer than the other two monothiols as judged by the minimum quantity of each molecule required to prevent cross-linking for a given reaction feed of TTT. Typically for the monothiol transfer agents, ME and MPD, with a VAc/TTT mole ratio of 100/3 a TTT/-SH mole ratio of 1/3 is required to avoid cross-linking i.e., a mole ratio of allyl group/-SH of 1/1. With the dithiol, DMEE, and a VAc/TTT feed mole ratio of 100/3, a TTT/DMEE mole ratio of 1/2 is sufficient to inhibit cross-linking. However, this corresponds to a mole ratio of allyl group/-SH of 1/1.25, i.e., a lower chain transfer efficiency than ME and MPD. Additional more precise work is needed to confirm this, but the result can be rationalized on the grounds that once one of the −SH groups in DMEE has participated in a transfer process, the remaining −SH group becomes attached to the terminus of a growing macromolecule, and on simple steric and mobility grounds, such groups might easily display a reduced reactivity. However, other side reactions might also be more favored with use of a dithiol e.g., cyclization reactions and disulfide formation, and of course the contribution of the IPE solvent in the overall chain transfer process is likely to dilute the differential behavior of the thiols.

Table 2. MALS/SEC Molar Mass Data for Branched PVAcs and PVOHs

	b-PVAc molar mass ($\times 10^{-3}$ g/mol)					*b*-PVOH molar mass ($\times 10^{-3}$ g/mol)		
	M_n	M_w	PDI	α[a]		M_n	M_w	PDI
1	7.8	183	24	0.33	1	7.2	95	13
2	31	155	5	0.33	2	16	109	7
3	11.5	438	38	*b*	3		*b*	
4	21	954	46	*b*	4	16	494	32
5	740	4600	6	*b*	5	*c*		
6	8.1	185	23	0.33	6	8.1	81	11
7	15	249	16	0.31	7	21	132	6
8	25	1200	47	*b*	8		*b*	
9	19	649	34	0.37	9	11	333	30
10	*b*	*b*	*b*	*b*	10	*c*		
11	22	276	12	0.30	11	14	95	8
12	22	1040	46	*b*	12	*c*		
13	14.6	400	27	0.30	13	*c*		
14	26	1240	48	*b*	14	*c*		

[a] Mark−Houwink α parameter. [b] Not measured. [c] Insoluble.

The molar mass distribution curves and molar mass elution volume plots for *b*-PVAc1−4 produced using ME as the transfer agent are shown in Figure 1, the data being obtained from the MALS/SEC instrument using THF as the eluent at 40 °C. The corresponding data for a linear PVAc reference polymer (M_w = 199 000) are also shown. Clearly the four branched samples have a broader and more complex molar mass distribution than that of the linear reference material, which itself demonstrates the profound influence of the TTT comonomer. The corresponding M_n, M_w and M_w/M_n (polydispersity index PDI) data computed from the curves are shown in Table 2. The broadening of the molar mass distribution curve is typical of what we[8−10] have seen using multifunctional comonomers as branching species and is consistent with complex chain-branching and chain transfer processes proceeding simultaneously with propagation in these polymerizations. In this context Steinke et al. have reported some elegant modeling studies.[14] The final product in each case is a complex mixture of macromolecules in terms of both the molar mass and the backbone architecture and we do not suggest for one moment that these materials can be compared directly with the structurally more uniform macro-

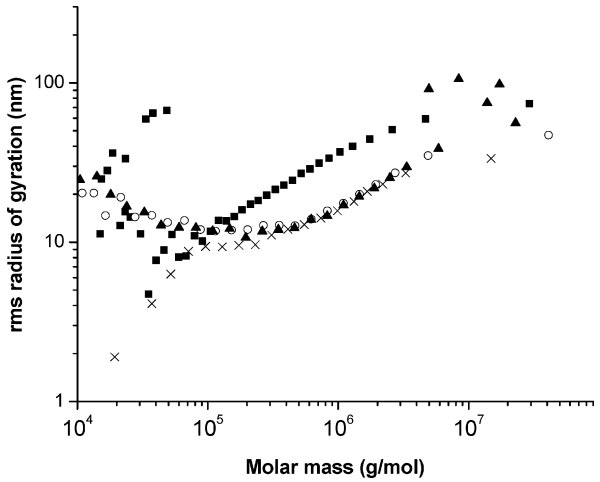


Figure 2. Rms radius of gyration vs molar mass for (■) linear PVAc reference polymer (M_w = 199 000), (×) *b*-PVAc1, (○) *b*-PVAc6, and (▲) *b*-PVAc11.

molecules with branched architectures prepared by more elaborate multistep chemistry.[7] However, that these macromolecules are branched essentially across the whole of the molar mass distribution is demonstrated by the molar mass vs elution volume curves (Figure 1), where the plots for *b*-PVAc 1−4 all lie to the upper right of the plot for the linear reference PVAc. The corresponding molar mass distribution curves and molar mass vs elution volume plots for samples *b*-PVAc 6−10 and *b*-PVAc 11−14 produced using TTT in combination with MPD and DMEE transfer agents respectively are very similar to the data in Figure 1 and are shown in the Supporting Information. Of course with these data we acknowledge that it is impossible to discount entirely that some microgel component is not present in the samples. However, our experience with a fairly broad range of branched vinyl polymers types[8c,d] is that samples containing microgel can give rise to handling and analytical problems as indicated earlier. None of these indicators have arisen in the generation of the data in Figure 1 nor in the corresponding data in the Supporting Information. The MALS/SEC instrument also allows computation of the root-mean-square (rms) radius of gyration of sample slices across the molar mass range and Figure 2 shows these plots for *b*-PVAc 1, 6, and 11 along with the plot for the linear reference PVAc. This group of samples was selected because of their similar M_w values. Clearly in the molar mass range where the scatter on the data is very small, the linear PVAc has a significantly larger rms radius of gyration at any given molar mass slice than that of the three branched samples, again confirming the branched and more globular structure of these macromolecules. From these data the Zimm branching factor,[15] g, for all three branched samples at molar mass slice 150 000 is ∼0.65, and this falls to ∼0.20 at molar mass slice 700 000 (in THF at 40 °C). Analysis of a representative spread of samples on a triple detector SEC instrument incorporating a viscometer detector also allows measurement of the corresponding Mark−Houwink α parameter[16] (Table 2). This is typically ∼0.30−0.35 for the branched samples with the corresponding experimentally determined value for the linear reference PVAc being 0.52 (in THF at 30 °C). A literature value for linear PVAc in THF at 35 °C is 0.71.[17] The variation of the latter from our own value is significant and may well have arisen from a compounding of factors. First, the intrinsic levels of branching in the two "linear" samples may differ. Second, somewhat different techniques have been used in the determinations each with its own errors, and finally the temperature at which the two measurements were made differs somewhat. In the present context however perhaps what is more important in not the absolute value of α for the "linear" reference PVAc but how the α values for the linear sample and the branched PVAcs compare. Clearly, irrespective of which value is considered for the linear sample, the data for the branched samples are consistently and significantly lower and totally consistent with their highly branched architecture.

Synthesis and Characterization of Branched PVOHs. The alcoholysis of the branched PVAcs using methanol (Scheme 1, step 2) proceeded very efficiently and recoveries of the corresponding PVOHs are good (Table 1). The high conversion of the −OAc to −OH groups is shown most clearly in the ^{1}H NMR spectra (Supporting Information) with the complete shift of the backbone C*H*OAc resonance from ∼5.0 ppm to that of the backbone C*H*OH at ∼3.9 ppm. At the same time the side chain acetate methyl hydrogen resonance at ∼2.0 ppm is also completely lost, and the characteristic resonance centered at ∼4.5 ppm assigned to the −O*H* hydrogen atom appears. Interestingly in the corresponding FTIR spectra (Supporting Information) of the PVOH there is a suggestion that some of the ester carbonyl band is retained, but if this is so the ^{1}H NMR data indicate that the residual acetate content must be very low. Nonetheless this could have an influence on, e.g., the water solubility. Also very importantly whereas the precursor PVAcs are readily soluble in $CDCl_3$, the derived PVOHs are insoluble, and the relevant ^{1}H NMR spectra of these were recorded in DMSO-d_6. Unambiguous confirmation from the ^{1}H NMR spectra of the retention of the branching TTT residues is again not possible because of the small and overlapping signals involved. However, the evidence from the corresponding FTIR spectra is quite definitive. Whereas the carbonyl ester stretching band in the *b*-PVAc at ∼1726 cm^{-1} is replaced by the strong and broad OH stretch at ∼3400 cm^{-1} in the *b*-PVOH, the TTT carbonyl band at ∼1685 cm^{-1} is essentially completely retained. In addition the wt % N in the *b*-PVOH samples typically increases by a factor of ∼1.5. Though this is lower than the theoretical value of ∼2 (see molar mass discussion below) the data probably falls within the experimental error, and clearly substantial N content is retained in the *b*-PVOHs.

The molar mass distribution curves and molar mass vs elution volume plots for samples *b*-PVOH 1, 2, and 4 prepared using ME as the transfer agent are shown in Figure 3 along with the corresponding data for a linear PVOH reference sample (M_w = 145 000). The samples were analyzed on a MALS/SEC instrument with aqueous 0.05 M $NaNO_3$ at pH 9 as the eluent at 40 °C. The empirical molecular formula of PVAc is $(C_4H_6O_2)_n$ and that of PVOH is $(C_2H_4O)_n$ so that an order of magnitude calculation suggests that alcoholysis of PVAc to PVOH should result in a halving of the molar mass. Indeed comparison of the M_w data (Table 2) for the *b*-PVAc samples and the *b*-PVOH samples derived from these essentially shows this to be the case, a correlation which not the least tends to give considerable credibility to the validity of the two sets of quite different "absolute" SEC molar mass analyses carried out. As with the corresponding precursor PVAcs the branched samples show considerably broadened and complex distributions relative to that of the linear reference material consistent with their branched architecture. The latter is confirmed in the molar mass vs elution volume plots. In the range of elution volumes where there is good correspondence of the data, those for the branched samples lie displaced to upper right of the data for the linear reference PVOH. The latter however has too narrow a molar mass distribution to allow a good comparison across the full elution volume range of the branched samples. The correspond-

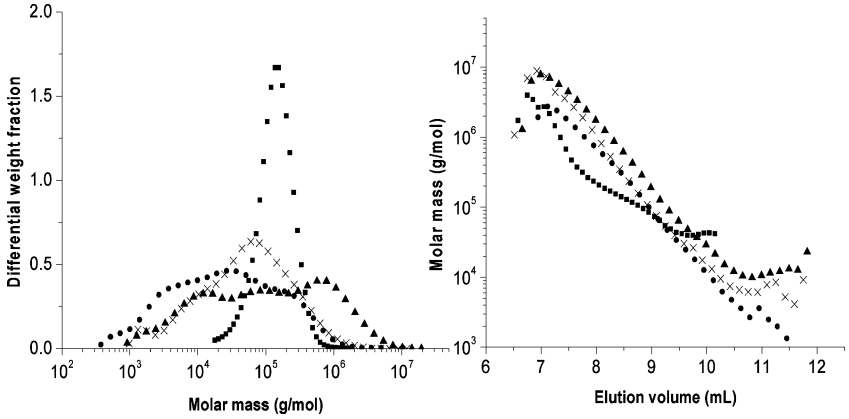


Figure 3. MALS/SEC molar mass distribution curves (left) and SEC molar mass vs elution plots (right) for (■) linear PVOH reference polymer (M_w = 145 000), (●) *b*-PVOH1, (×) *b*-PVOH2, and (▲) *b*-PVOH4.

ing data for samples *b*-PVOH 6, 7, and 9 are very similar to the above set and are shown in the Supporting Information.

Interestingly, and initially to our surprise, the PVOH samples which in principle might be expected to be the most branched, i.e., *b*-PVOH5, 10, and 14, as a result of the higher level of TTT in the polymerization mixtures, show rather poor solubility in water. Likewise samples *b*-PVOH 12 and 13 prepared with the difunctional transfer agent DMEE. Since all of the precursor branched PVAcs corresponding to these branched PVOH samples are readily soluble in e.g. THF, the poor water solubility of these PVOHs cannot be attributed to cross-linking. The branched PVOHs are of course not simply poly(vinyl alcohol) homopolymers but are in effect copolymers involving TTT-derived segments. Since the latter almost certainly have some increased level of hydrophobicity associated with them, this may well play a role in determining the water solubility of these branched species. Likewise any residual acetate groups will increase the overall hydrophobicity. However notwithstanding this it is important to recall that the grades of linear PVOH that are marketed as '100% hydrolyzed' are also *insoluble* in cold water, and only prolonged boiling in water breaks down the tight internal H-bonding structure allowing these macromolecules to eventually dissolve. It may be therefore that the poor water solubility of *b*-PVOH 5, 10, and 12−14 is in part due to similar internal H-bonding within the globular architecture of these macromolecules. It is also possible that a similar situation may prevail with the PVOH comb materials prepared by Stenzel et al.[7b] but their paper does not report specifically the response of their materials to water. Water insolubility also arises of course with a number of natural polysaccharides despite their high −OH group content, and with particular proteins and polypeptides.

The MALS/SEC data on the water-soluble branched PVOHs allows evaluation of their rms radii of gyration across the molar mass range, and the variation of this parameter is shown for *b*-PVOH 4 and 9 in Figure 4 together with data on the linear reference PVOH. The latter plot is rather oddly shaped. These data are derived from the corresponding molar mass vs elution volume plots in Figure 3 (right) where the line for the linear PVOH reference displays a "wave" on what would normally be the linear portion of the plot. A possible explanation for this is that a molar mass dependent sorption chromatographic separation mechanism might be operating in addition to the normal size exclusion process. Aqueous phase SEC analysis of synthetic polymers and certainly aqueous phase MALS/SEC analysis is a relatively new instrumentation technique and is far less routine and straightforward than the corresponding

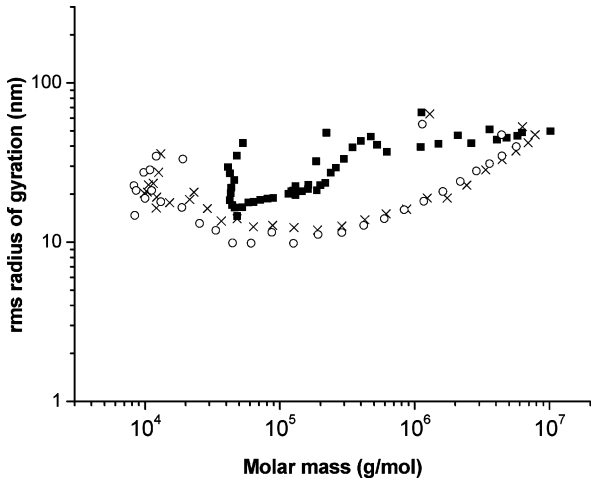


Figure 4. Rms radius of gyration vs molar mass for (■) linear PVOH reference polymer (M_w = 145 000), (×) *b*-PVOH4, and (○) *b*-PVOH9.

organic phase procedure. In the case of PVOH which has significant amphipathic characteristics stationary phase sorption might arise fairly readily and exhibit an analyte molar mass dependence. Also self-aggregation equilibria might provide additional complexity. In contrast, the behavior of the branched PVOHs seems more conventional and this may be due to the more globular nature of these molecules with a lower tendency for polymer−stationary phase and polymer−polymer interactions to arise. Overall, the much smaller dimensions of the branched samples at a given molar mass relative to the linear reference confirms the branched and more compact architecture of these macromolecules.

Reacetylation of Branched PVOHs. Since it was not possible from our analytical data to quantify the number of branches in the PVOH samples, and a detailed comparison of molar mass data for PVOHs and PVAcs may be misleading, it was decided to reacetylate representative branched PVOH samples and compare the products with the respective original branched PVAc precursors. We argued that if significant cleavage of the TTT branching units occurred during alcoholysis of each branched PVAc then the molar mass characteristics of each of the reacetylated branched PVOHs would differ considerably from those of the corresponding precursor branched PVAcs. The reacetylation reactions went well and the ^{1}H NMR spectra of the products (Supporting Information) show complete loss of the resonances associated with the backbone C*H*OH H atom and that of the −O*H* H atom. These losses are accompanied by the reappearance of the resonances associated

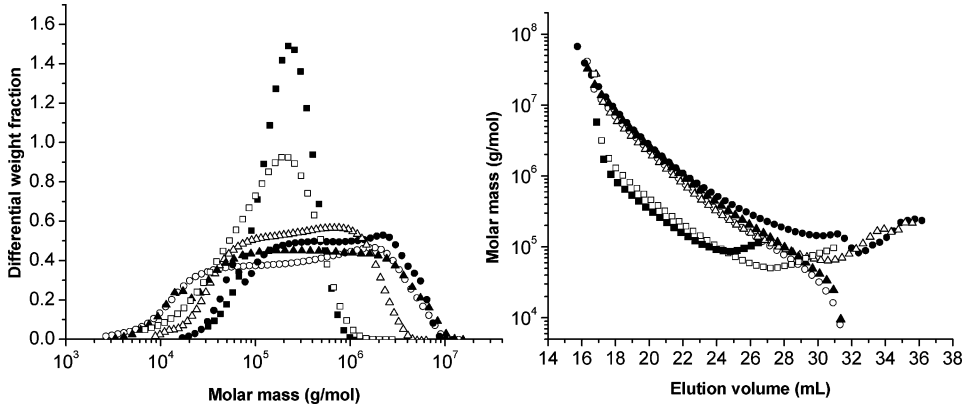


Figure 5. MALS/SEC molar mass distribution curves (left) and SEC molar mass vs elution plots (right) for (□) linear PVAc reference polymer (M_w = 199 000), (■) acetylated linear PVOH reference polymer (original M_w = 145 000), (○) *b*-PVAc4, (●) reacetylated sample *b*-PVOHAc4, (△) *b*-PVAc9, and (▲) reacetylated sample *b*-PVOHAc9.

with the backbone C*H*OAc H atom and that of the side chain acetate methyl H atoms. The MALS/SEC molar mass data for two reacetylated samples *b*-PVOHAc 4 and 9 and their original precursors *b*-PVAc 4 and 9 are shown in Figure 5 together with the data for the linear PVAc reference material and the acetylated derivative of the linear PVOH reference material (*note* this acetylated PVOH is not derived from the PVAc reference polymer but from the PVOH reference sample). Very rewardingly, the molar mass distribution curves for the two reacetylated branched PVOHs are remarkably similar to their respective branched PVAcs precursors. Also the breadth and complexity of the distributions relative to that of both the linear PVAc reference and the acetylated linear PVOH reference are retained. The molar mass vs elution volume plots for the two reacetylated samples and their branched PVAcs precursors all tend to lie closely on top of each other and are also displaced to the upper right of the plots for the two linear reference materials. These results demonstrate conclusively the considerable similarity between each corresponding pair of branched PVAcs despite the fact that one of each pair has undergone prolonged chemical processing involving alcoholysis, workup, isolation, reacetylation, workup, and isolation. The data also confirm that the original branching architecture present in the precursor PVAc samples is carried through into the PVOHs and thereafter into the reacetylated samples.

Conclusions

Conventional free radical co-polymerization of VAc with the trifunctional comonomer TTT in isopropoxy ethanol in the presence of thiol chain transfer agents allows the facile synthesis in high yield of branched PVAcs. Absence of any significant vinyl hydrogen resonances in the ^{1}H NMR spectra suggest that the TTT is efficiently co-polymerized and that average branching levels are in the range one branch per 16/17 VAc residues and one branch per 6/7 VAc residues. The % N content in the samples and in particular the FTIR spectra reinforce this conclusion. Significant branching is confirmed with extensive molar mass distribution data from MALS/SEC analysis and comparison with a linear reference PVAc. Alcoholysis of the branched PVAcs using alkaline methanol yields the corresponding branched PVOHs in high isolated yield. A very high level of conversion of acetate to hydroxyl groups is demonstrated in the relevant ^{1}H NMR spectra. MALS/SEC data, FTIR spectral analyses, and % N microanalytical data confirm that the branching TTT residues are stable and that the branched architectures of the PVAcs precursors are retained in the derived PVOHs. Furthermore, reacetylation of the latter has been carried out very efficiently, and the MALS/SEC analytical data of the products confirm that the original branching architectures are retained throughout the entire chemical modification cycle. In particular, this confirms that a facile synthesis of branched PVOHs has been achieved.

Since the methodology we have evolved is relatively straightforward, we believe that larger samples could readily prepared in the laboratory to allow broader physicochemical characterization (e.g., rheological and viscometric studies, surface activity and other interfacial properties, etc.) of branched PVOHs to be carried out. Furthermore, linear PVOHs are reported to be produced on an industrial scale using elegantly integrated engineering in which a continuous polymerization reactor feeds a continuous alcoholysis reactor.[4] The presently reported methodology for producing branched PVOH variants is not synthetically complex and demanding. It involves only relatively minor adjustments to the routine chemistry of linear PVOH synthesis. This methodology therefore offers excellent prospects for scale-up within existing plant, and hence for making branched PVOHs available in exploitable quantities for a broad spectrum of would-be commercial and industrial users.

Acknowledgment. R.B. is grateful to the UK DTI for the provision of a Research Assistantship within the B-Vinpol project in collaboration with our industrial partners in Unilever Research and Industrial Copolymers led by Dr P. Findlay. We also appreciate the access to the Triple Detector SEC instrument made available to us by Professor S. Armes of the University of Sheffield, U.K., and the help of Dr. D. C. Vo.

Supporting Information Available: Figures showing representative ^{1}H NMR and FTIR spectra along with additional MALS/SEC data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Lennart Marten, F. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; J. Wiley and Sons: New York, 1989; Vol. 17, pp 167−198.

(2) Li, H.; Zhang, Y.; Chen, X.; Shi, K.; Yuan, Z.; Liu, B.; Shen, B.; He, B. *React. Funct. Polym.* **2004**, *58*, 53−63.

(3) (a) Burchard, W. *Adv. Polym. Sci.* **1999**, *143*, 113−194. (b) McLeish, T. C. B.; Milner, S. T. *Adv. Polym. Sci.* **1999**, *143*, 195−256. (c) Brenner, A. R.; Voit, I.; Massa, D.; Turner, S. R. *Macromol. Symp.* **1996**, *102*, 47−54.

(4) Mukul, B.; Mazumdar, A.; Mitra, P. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; J. Wiley and Sons: New York, 1989; Vol. 17, pp 393−468.

(5) Grcev, S.; Schoenmakers, P.; Iedema, P. *Polymer* **2004**, *45*, 39−48.
(6) Rimmer, S.; Collins, S.; Sarker, P. *Chem. Commun.* **2005**, 6029−6031.
(7) (a) Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C. *Chem. Commun.* **2004**, 1546−1547. (b) Bernard, J.; Favier, A.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. *Polymer* **2006**, *47*, 1073−1080. (c) Bernard, J.; Favier, A.; Zhang, L.; Nilasaroya, A.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. *Macromolecules* **2005**, *38*, 5475−5484.
(8) (a) O'Brien, N.; McKee, A.; Sherrington, D. C. *Polym. Commun.* **2000**, *41*, 6027−6031. (b) Costello, P. A.; Martin, I. K.; Slark, A. T.; Sherrington, D. C.; Titterton, A. *Polymer* **2002**, *43*, 245−254. (c) Isaure, F.; Cormack, P. A. G.; Sherrington, D. C. *J. Mater. Chem.* **2003**, *13*, 2701−2710. (d) Isaure, F.; Cormack, P. A. G.; Sherrington, D. C. *Macromolecules* **2004**, *37*, 2096−2105. (e) Baudry, R.; Sherrington, D. C. *Macromolecules* **2006**, *39*, 1455−1460.
(9) Isaure, F.; Cormack, P. A. G.; Graham, D. C.; Sherrington, D. C.; Armes, S. P.; Butun, V. *Chem. Commun.* **2004**, 1138−1139.
(10) Camerlynck, S.; Cormack, P. A. G.; Sherrington, D. C.; Saunders, G. J. *Macromol. Sci., Part B: Phys.* **2005**, *44*, 881−895.
(11) Ohnaga, T.; Sato, T. *Polymer* **1996**, *37*, 3729−3735.
(12) Berger, K. C.; Brandrup, G. *Polymer Handbook*, 3rd ed.; Brandrup, G., Immergut, E. H., Eds.; J.Wiley and Sons: New York, 1989; Chapter II, p 141.
(13) Collins, S.; Rimmer, S. *Rapid Commun. Mass Spectrom.* **2004**, *18*, 3075−3078.
(14) Gretton-Watson, S. P.; Alpay, E.; Steinke, J. H. G.; Higgins, J. S. *Chem. Eng. Sci.* **2006**, *61*, 1421−1433.
(15) Zimm, B. H.; Stockmeyer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301−1314.
(16) Kurata, M.; Tsunashima, Y. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; J. Wiley and Sons: New York, 1989, Chapter VII, p 2.
(17) See ref 16, p 13.

MA061221D