Preparation of highly branched poly(vinyl acetate) by transfer to allylic carbonate comonomers†

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Copolymerization of vinyl acetate with allyl carbonates that contain isopropyl groups yields highly branched poly(vinyl acetates).
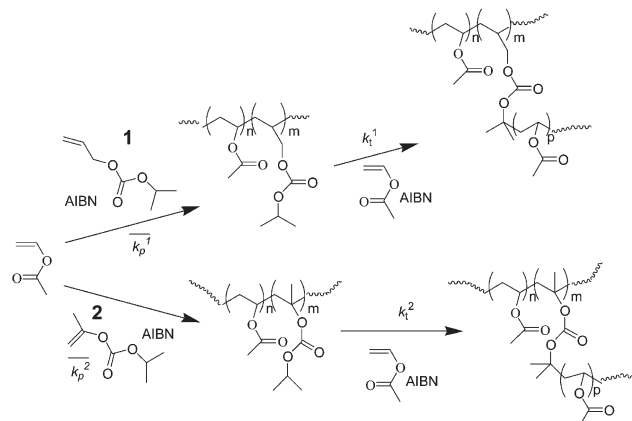
There is currently a great deal of interest in the synthesis and properties of highly branched polymers. Recent work has shown that in radical polymerizations containing difunctional monomers the branched architecture can be maintained and gelation can be prevented by either the addition of transfer agents[1] or by employing controlled polymerization techniques.[2,3] Also highly branched polymers can be prepared by incorporating monomers that contain groups that are initiators or transfer agents in controlled radical polymerizations.[4-6] However, monomers derived from alkenes that do not contain groups that are able to stabilize the propagating radical are not very amenable to controlled radical polymerizations; although the use of xanthates has been reported for controlling the polymerization of vinyl acetate (VAc) to prepare PVAc stars.[7] In radical polymerizations thiols are the most often reported chain transfer agents that are used to add chain end functionality and control molecular weights and/or gelation.[1] However, the rates of transfer from propagating radicals derived from monomers such as VAc (*i.e.* monomers that do not provide π-delocalization stabilization to the propagating radical) are too high to be used in these polymerizations, unless their concentration can be controlled in a continuous feed into the reaction vessel. PVAc and the hydrolysed material (poly vinyl alcohol) have many uses that involve their rheological properties and properties as agents for stabilizing dispersions. Both areas might be enhanced by controllable branching. In this communication we report the synthesis of highly branched PVAc by incorporating comonomers (allyl carbonates), which include groups with significant transfer constants with the propagating VAc radical. The inclusion of the isopropyl group in these monomers should provide rates of transfer that are low enough to allow chain propagation to take place. Transfer by abstraction of the isopropyl hydrogen generates a branch point following copolymerization of the allyl group, as shown in Fig. 1. To our knowledge highly branched polymers composed of repeat units derived from monomers (such as VAc) that propagate by non-stabilized radicals have not been reported previously. The high reactivity of the propagating radical in

polymerizations of VAc should allow it to be copolymerized with allyl carbonates.

Abstraction of hydrogen atoms from compounds deliberately added to radical polymerizations (chain transfer agents) is a well practised technique, which is used to control molecular weight and to add chain end functionality. In this technique the primary radical is terminated and a new radical reinitiates the kinetic chain. The propagating VAc radical has a substantial transfer constant, k_{tr}, (rate of transfer = k_{tr} [P•][CA], where [P•] = concentration of the propagating radical and [CA] = concentration of the chain transfer agent) with many compounds that are often regarded as inert in similar polymerizations of methacrylates, acrylates and styrene-derivatives (*e.g.* see ref. 8). Thus, here we report the discovery that highly branched PVAc can be produced, as illustrated in Fig. 1, by including allyl carbonate monomers into the polymerizations of VAc.

Intitially, copolymerizations of VAc and **1** were carried out at 60 °C in butyl acetate as solvent. Each of these polymerizations produced insoluble cross-linked material indicating that the carbonate monomer did copolymerize with VAc and that transfer to the comonomer also occurs during the timescale of the polymerization. Gelation then occurs by bimolecular combination (termination by coupling of two radicals) of the propagating PVAc chain branches.

In order to prevent macroscopic gelation it is necessary to increase the rate of transfer so that the transfer reactions become the main termination processes and are the dominant termination process rather than termination by bimolecular termination. An increase in the rate of transfer can be achieved by either increasing the polymerization temperature or increasing the concentration of

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Fig. 1 Scheme showing copolymerization of VAc with allyl carbonate branching monomers and transfer to 2-propyl moieties.
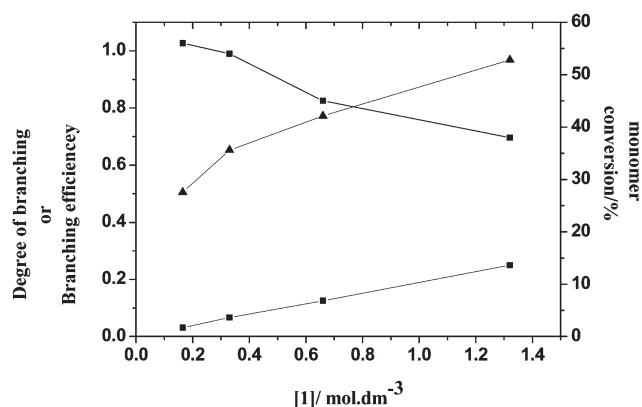
Fig. 2 Colymerization of VAc with **1** ■ conversion, after 1.5 h at 150 °C, ▲ branching efficiency; ■ degree of branching.

the transfer agent. In order to minimize gelation the former method requires the addition of another non-polymerizable chain transfer agent. On the other hand, the temperature dependence of the rates of transfer by hydrogen abstraction is generally higher than that of bimolecular termination so it should be possible to polymerize VAc at a temperature at which the dominant termination reaction is transfer rather than bimolecular termination. Both of these modifications were effective. Thus, increasing the polymerization temperature, to 150 °C, in the absence of any other transfer agents produced soluble (non-cross-linked) materials. Also, soluble materials were obtained by adding isopropanol to the reaction mixture in polymerizations carried out at 60 °C.

Polymerization performed at 150 °C, in the absence of isopropanol, gave products that were completely free of insoluble material, and Fig. 2 and Fig. 3 show the effects of adding **1** or **2** to the polymerizations of VAc.

There is a substantial decrease in final monomer conversion (after a reaction time of 1.5 h) as the concentrations of **1** or **2** are increased. This effect is a good indication of the involvement of these comonomers in the polymerizations. The decrease in conversion is derived from the decrease in average propagation rate constant, k_p, (rate of propagation = k_p [P·][M], where [M] = the instantaneous monomer concentration) due to the lower reactivity of the propagating radicals derived from **1** or **2**. The
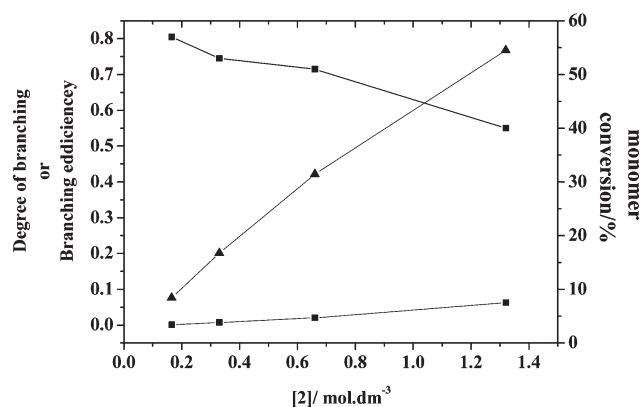

Fig. 3 Colymerization of VAc with **2** ■ conversion, after 1.5 h at 150 °C, ▲ branching efficiency; ■ degree of branching.

Table 1 Results from polymerizations carried out at 150 °C

CM	[CM]/mol dm^{-3}	M_n/g mol^{-1}	M_w/g mol^{-1}	PDi
—	0	3990	12 815	3.2
1	0.165	4250	25 200	5.9
1	0.33	4280	51 700	12.1
1	0.66	5120	104 200	20.4
1	1.32	5720	77 650	13.6
2	0.165	3850	12 600	3.3
2	0.33	2850	11 800	4.1
2	0.66	2850	12 150	4.3
2	1.32	2350	10 990	4.7
3	1.32	12 650	86 300	6.8
4	1.32	4700	12 070	2.6

architecture of these polymers is defined by the degree of branching and the progress of the polymerization is defined by the branching efficiency. Both parameters can be obtained from ^{1}H NMR spectra. The branching efficiency is expressed as the number of isopropyl groups containing a branch per repeat unit of **1** or **2** and the degree of branching is expressed as the number of branch points per repeat unit.

Branching efficiency increases as the concentrations of the branching comonomers increase. This observation is expected for a polymerization in which the propagation events compete with the transfer reaction that leads to branching. Thus, as the concentration of **1** or **2** increases the absolute rate of transfer increases as the average rate of propagation decreases. This increase in branching efficiency produces an increase in the degree of branching above that expected from considering the increase in concentration of **1** or **2** alone.

Table 1 gives the nominal molecular weight data derived from size exclusion chromatography (SEC) measurements in THF, for the series of polymers produced in the presence of either **1** or **2**. The use of the high polymerization temperature produced a control sample, prepared in the absence of either comonomer (CM), which had a low molecular weight. The addition of **1** to the polymerization mixture tends to broaden the molecular weight distribution and increases the molecular weight averages by increasing the fraction of higher molecular weight material.

The nominal molecular weight distributions obtained in the presence of **1** are shown in Fig. 4 and are clearly polydisperse and broad. On the other hand the polymerizations conducted in the presence of **2** gave unimodal nominal molecular weight distributions.

Thus these data clearly show that **2** is less effective as a branching comonomer than **1** since the addition of **2** appears not
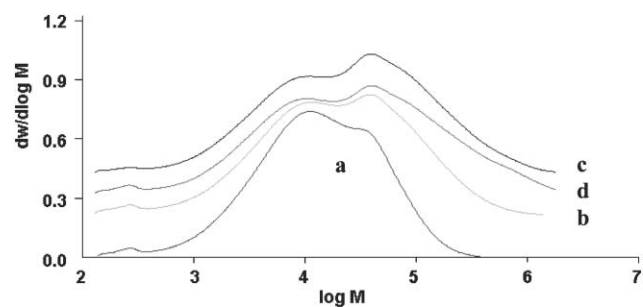

Fig. 4 SEC nominal molecular weight distributions: copolymerization of VAc and **1** at 150 °C [**1**]/mol dm^{-3} **a** = 0.165, **b** = 0.33, **c** = 0.66, **d** = 1.32.

to result in broadening of the molecular weight distribution; an increase in polydispersity index (weight average molecular weight/number average molecular weight (M_w/M_n)), PDi. Broadening of the molecular weight distribution is expected for any polymerization that progresses by either transfer to monomer or polymer.[9] Fig. 2 and Fig. 3 clearly show that rates of transfer to the isopropyl group are similar for both **1** and **2**: similar rates of transfer are reflected in similar values of branching efficiency. Therefore, the failure of **2** to broaden the molecular weight distribution is probably due to the lower reactivity in the propagation step of the isopropenyl carbonate group when compared to the allyl carbonate group.

In order to further confirm these results a second set of branching agents were also studied, carbonic acid allyl ester 2-isopropoxy-ethyl ester (**3**) and carbonic acid isopropenyl ester 2-isopropoxy-ethyl ester (**4**), in which ethyloxy groups were inserted between the carbonate group and the isopropyl group. The PDi data, shown in Table 1, confirmed that the polymerization with the allyl carbonate comonomer, **3**, was more effective than polymerization with the isopropenyl carbonate comonomer, **4** (*i.e.* the PDi produced when **3** was used is significantly higher than when **4** was used). The branching efficiency was 0.76 and 0.92 respectively for **3** and **4**.

An alternative to the use of increased polymerization temperature as a means of minimizing gelation is to add a non-polymerizable chain transfer agent. The latter technique also offers the advantage that if this additive contains useful functionality it will be placed at the chain ends of the final product. Polymerizations were therefore carried out in the presence of **1** and isopropanol at 60 °C.

The low molecular weight fractions produced as a consequence of carrying out the polymerizations at high temperatures (150 °C) meant that the evaluation of absolute molecular weight data, using triple detection apparatus, on the previous set of experiments was not possible. However the higher molecular weight averages produced at 60 °C in this set of experiments did allow us to determine absolute molecular weight distributions, using SEC with light scattering, viscometric and refractive index detectors. All of the polymerizations carried out in the presence of 2-propanol produced soluble products with no gel formation. In previously reported work we showed that the polymerization of VAc in 2-propanol produces oligomeric products that are useful as reactive precursors.[9] However, Table 1 shows that the addition of **1** to polymerizations of VAc in isopropanol produces high molecular weight polymers with broad molecular weight distributions. The triple detection procedure also allows us to make plots of intrinsic viscosity against log (molecular weight) (log M). The gradients of these plots give the exponent of the Mark–Houwink equation (α)[10] and provide a semi-qualitative measure of the degree of branching. It is widely accepted that linear polymers in good solvents give values of α approaching 1 and the limiting value for a linear polymer at the theta point (*i.e.* the minimum solvency conditions to maintain the polymer in solution) is 0.5. Thus polymers dissolved in good solvents that give values of close to or

Table 2 Results from polymerization of VAc in the presence of **1** at 150 °C

[VAc]	[1]	Conversion (%)	M_n	M_w	PDi	α
5.4	0.17	63	15.8	78.0	4.9	0.49
5.4	0.33	52	10.2	102.2	10.0	0.44
5.4	0.66	75	11.1	85.5	7.7	0.47
4.3	0.13	66	30.1	322.9	10.7	0.46

less than 0.5 do so because their architectures are more compact (*i.e.* more branched in this case) than linear equivalent polymers.[11] Each of the polymers prepared in the presence of isopropanol and **1** gave $\alpha < 0.5$ as shown in Table 2. These data are strong indications of the branched nature of these polymers. Thus although, unlike in the polymers prepared at higher temperature we were unable to probe and quantify the degree of branching by using NMR spectroscopy, the viscometry of these polymers shows that they are not linear and are clearly more branched than polymerizations carried out in the absence of **1**.

Thus we have shown that the allyl monomers used here are suitable comonomers for controlling the branching of VAc and other monomers that polymerize by propagating radicals that are not stabilized by π-delocalization. Whilst transfer to monomer in VAc polymerizations is well-known and produces branched polymers, as far as we are aware this is the first report of copolymerizations in which monomers are deliberately added to control the branching of these polymers. Control over branching in this way is expected to produce materials with interesting rheological and mechanical properties and work is underway on studying these properties. We have also used copolymerization with isopropyl functional allyl carbonates to prepare other branched polymers from other monomers that also polymerize *via* non-stabilized radicals, such as *N*-vinyl pyrrolidinone and vinyl cyclopropanes, and results from these polymerizations will be reported in full in due course.

Notes and references

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