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Precision and Control in Polymer Synthesis Why It's Important and Some Recent Examples of How to Do It

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SUMMARY: This paper discusses some of the reasons why precision and control in polymer synthesis is of importance. By way of illustration it describes in outline recent results from the authors' laboratories in three areas. Namely; the controlled syntheses of poly(arylene vinylene)s and the influence of cis/trans vinylene content on luminescence in such polymers; the living polymerisation of highly functionalised polymers in water and the regulation of the crystallisation of calcium carbonate from water by the resultant well-defined water soluble polymers; and a simple route to hyperbranched polymers and the influence of the structure and topology of the products on solution properties. In each case the influence of control of architecture on properties will be discussed.

Introduction

Aphorists tell us that we live in the "Age of Plastics" and it is true that plastics influence the lives of most of the inhabitants of the world. This is a truly remarkable state of affairs, which happened relatively recently and very rapidly. Thus the ubiquitous polyethylene only saw the light of day in 1933 but has experienced a spectacular growth in production and use over the last half century.(1) The methods of making and manipulating it have become increasingly sophisticated and the areas of application have spread from candle wax, wire insulation, washing-up bowls and buckets in the early days to high quality materials suitable, for example, for hauling elevators and even replacing

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worn body parts.[1-3] The history and intellectual base of the subject have been extensively reviewed.[4,5]

In the last couple of decades specialist plastic materials have become increasingly important and this trend seems likely to continue although commodity bulk polymers will continue to be improved and extensively used. The newer materials often have very precisely defined properties and functions and this requires that they have well defined structures. Whereas most of the polymers in common use are made using only a handful of well-known reactions; including vinyl additions, esterifications, amidations, and isocyanate and phenol/formaldehyde chemistries; these newer materials often require new methods of synthesis. Consequently many techniques and reagents have been introduced from the organic and organometallic chemists' armoury into the field of polymer synthesis.

In this paper we illustrate this theme with three examples chosen from recent work in our laboratories.

1. The cis/trans ratio in poly(arylene vinylene)s.

Poly(arylene vinylene)s, PAVs, have been known for a long while.[6-8] Since the discovery of electroluminescence in these polymers [9] they have attracted enormous interest as the materials of choice for use as active layers in polymer based light emitting diodes. The field has been reviewed recently and it is clear that most effort has been focused on poly(paraphenylene vinylene), PPV, and its derivatives.[10] PPV is generally obtained via the precursor route outlined in figure 1.

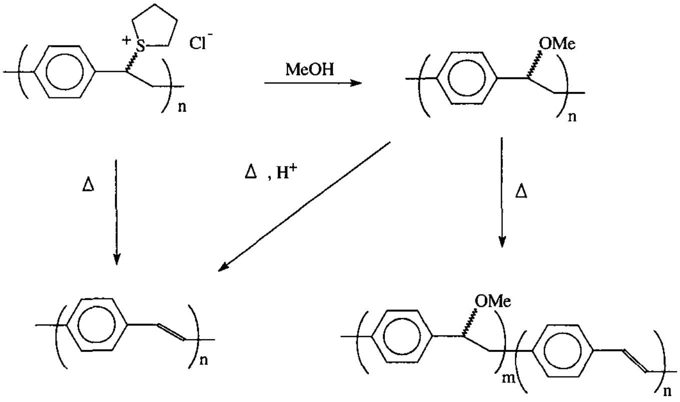

Figure 1. Precursor route to PPV.

This route has been intensively investigated and developed and modified so as to give access to a very wide range of PAVs. Some years ago we established an alternative route to a PAV namely, poly(4,4'-diphenylene diphenylvinylene) (PDPV), using the McMurry coupling of a ketone. The product polymer, PDPV, was soluble and therefore relatively easily processible and displayed interesting photo and electroluminescence.[7,11] The process is summarised in figure 2.

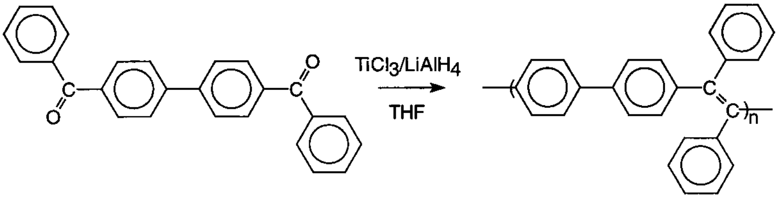

Figure 2. The synthesis of poly(4,4'-diphenylene diphenylvinylene) via Murry coupling

This result was interesting but raised other problems in that we had no analytical technique that would allow us to define the cis/trans frequency and distribution in this polymer. When this question thrust itself upon our attention it appeared that very little was known concerning the effect of chain microstructure on luminescence efficiency in PAVs. The approach to solving this problem, which we adopted, was to devise an alternative route to the same basic polymer structure in which the cis/trans distribution was controlled. We started with 4-bromobenzophenone, which undergoes McMurry coupling to give both cis- and trans-4,4'-dibromotetraphenylethene, the isomers were separated by fractional crystallisation and unambiguously identified by X-ray crystallography.[12] This new monomer was used in Yamamoto coupling[13] in an alternative route to PDPV, see figure 3.

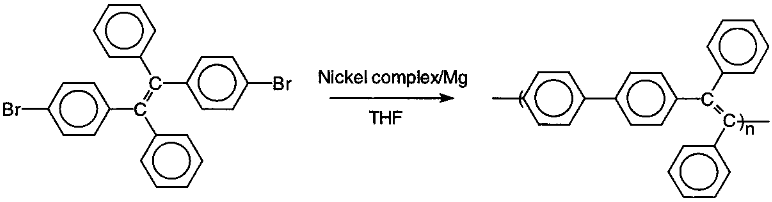

Figure 3. Yamamoto coupling of trans-4,4'-dibromotetraphenylethene to give trans-poly(4,4'-diphenylene diphenylvinylene).

It is, of course, obvious that since we have prepared and purified both the cis and the trans isomers of 4,4'-dibromotetraphenylethene we can control the relative proportions of cis and trans vinylene units in the polymer backbone simply by varying the composition of the monomer mixture. Suzuki coupling is another transition metal mediated coupling reaction which is beginning to be explored for use in polymer synthesis,$^{14)}$ and exactly the same idea for control of cis/trans vinylene content can be applied to the coupling of 4,4'-dibromotetraphenylethenes with arylene bisboronic acids, this is illustrated in figure 4.

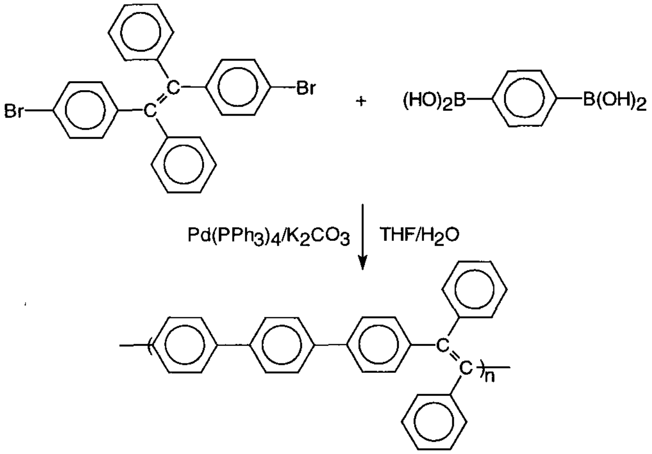

Figure 4. Suzuki coupling of trans-4,4'-dibromotetraphenylethene with benzene-1,4-diboronic acid to give trans- poly(4,4'-paratriphenylene diphenylvinylene).

In this way a whole family of PAVs can be synthesised in which we have control over the cis/trans vinylene content and the size and geometry of the arylene repeat unit. It turns out that the polymer chain microstructure has a considerable influence over the properties of the PAV. This is illustrated by the data presented in table 1 which shows that the cis/trans content in this particular PAVs has a marginal effect on the photoluminescence emission wavelength but has a very marked effect on the solid state photoluminescence efficiency which peaks at a cis:trans ratio of about 50:50 in this particular polymer and in the three other systems investigated to date. The difference between the solid state photoluminescence efficiency for a PAV with an all cis or all trans vinylene content and the analogous systems with a roughly 50:50 cis:trans ratio approaches a factor of two.

This illustrates the potential importance of precision and control in synthesis in this class of polymers.

Table 1 Photoluminescence data for poly(tetra-p-phenylene diphenylvinylene)s.

Sample	% *cis* isomer	Photoluminescence	
		efficiency (%)	λ_{max} (nm)
1	97	28.6	524
2	62	30.1	533
3	48	53.5	520
4	32	32.5	521
5	2	30.7	496

2. Living polymerisation of highly functionalised polymers in water and regulation of the crystallisation of calcium carbonate.

Natural inorganic/organic composites serve a variety of functions and are frequently remarkable materials (e.g. bones, teeth, endo- and exo-skeletons). One of the mechanisms by which they are believed to be produced involves the deposition of a polymer matrix which is subsequently covered with mineral.15) The most widely utilised mineral in bioinorganic structures is calcium carbonate.16) In Nature cells control both polymer and mineral deposition via concentration, electrochemical, proton (pH) and redox gradients. A question which the work referred to in this section attempts to address is the possibility of building entirely synthetic organic/inorganic composite materials in an analogous way. Many organic/inorganic composites have been prepared by in situ inorganic precipitation within organic matrices, examples include, slow diffusion of ammonium carbonate vapour into a calcium chloride solution doped with aliquots of proteins,17) addition of water to a solution of a polymer and metal alkoxide in a suitable solvent18) or by intercalation of soluble organic substances into a preformed mineral matrix such as layered silicates.19) The matrix for the mineralisation of inorganic crystals can also be an organic monolayer. Amphiphilic monolayers can control the nucleation of crystals and stabilise the resulting nuclei in a preferred orientation.20) Also the presence of organic additives is known to have a significant effect upon the morphology of crystals grown from supersaturated solutions.21) At low concentrations polymers in solution are habit modifiers for crystal growth, by selective adsorption to and poisoning of specific growth faces.

In order to study the interactions between the polymer and the mineral it is desirable to produce water-soluble polymers with well-defined molecular weight distributions, a process which requires living polymerisation of functionalised monomers. We have used the well defined ring opening metathesis polymerisation (ROMP) initiators developed by Shrock$^{22)}$ and Grubbs$^{23)}$ in living polymerisations of a series of functionalised norbornene monomers to make well defined water soluble polymers. Examples of the process are shown below. Thus in figure 5 the polymerisation, hydrogenation and hydrolysis of the exo,exo-, endo, endo- and exo,endo-isomers of the 5,6-methylcarboxylates of norbornene is outlined. This process gives access to a set of well defined water soluble polymers carrying two sodium carboxylate substituents per repeat unit in a well defined geometrical relationship and, since the Schrock initator gives living ROMP, this approach allows control of the molecular weight and its distribution as well.

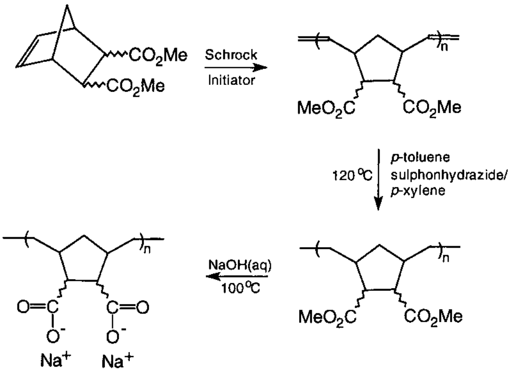

Figure 5. Route to well defined functional water soluble polymers (see text)

Another type of monomer we have examined carries the functional group at the end of a spacer unit that separates it from the polymerisable norbornene residue and the polymer backbone. Three examples of this type of monomer are shown in figure 6. These monomers formed micelles in water and underwent living ROMP when a solution of the Grubbs' ruthenium carbene initiator in chloroform was introduced.

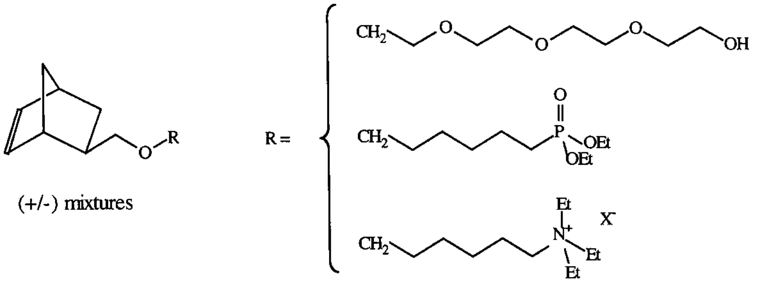

Figure 6. Norbornene monomers in which the functional group is separated from the norbornene by a spacer

The data shown in table 2 and figure 7 is illustrative of the evidence for living polymerisation.

Table 2. GPC data (in chloroform, relative to polystyrene standards) for the system reported in Figure 6..

[M]:[I]	47	88	125	165	283	390
M_n	29,100	37,800	65,000	74,400	122,800	207,100
PDI	1.13	1.24	1.17	1.14	1.39	1.15

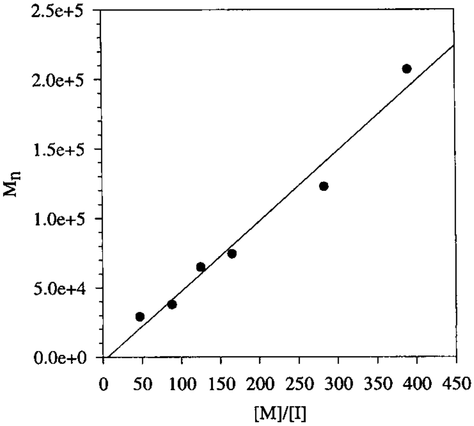

Figure 7. Plot of number average molecular weight (GPC in chloroform, polystyrene standards) versus monomer to initiator ratio ([M]/[I]) for the monomer with a ($CH_2CH_2O)_4H$ side chain (see Figure 6).

We have studied many well-defined water-soluble functional polymers, of the kind obtained via the routes outlined above, in calcium carbonate crystal growth assays. In this process an aqueous solution of the polymer under investigation is added to a solution of calcium hydrogen carbonate under standard conditions and the crystals which form are analysed by microscopy and diffraction methods. Calcium carbonate has three crystalline forms, calcite, aragonite and vaterite. The first of several requirements for making an inorganic/organic composite via this approach is that the polymer additive results in preferential growth of one, and only one, of the three crystalline forms and that the crystals have the same shape and size. Sadly, for many of the water-soluble polymers that we have examined the degree of control over crystal growth is non-existent or negligibly small; however, happily, in some cases crystal form, size, shape and nucleation density can all be controlled. An example of this is shown in figure 8, in this case the polymer used had the structure shown in the bottom left hand corner of figure 5 in which the sodium carboxylate units have an anti geometry with respect to the ring (that is it was derived from the exo,endo-monomer). In the crystal growth assay the ratio of calcium ions to carboxylate units was 10:1 in all cases. The crystals were grown under identical conditions for the same period of time. The sample shown in the top left-hand corner was grown from a solution containing polymer with a number average molecular weight (Mn) of 6000, that in the top right-hand corner used a polymer of Mn 65,000 and that in the bottom left-hand corner had a Mn of 147,000. All the crystals are of calcite, all have the same shape and are modified on the same crystal face. The size distribution is also controlled.

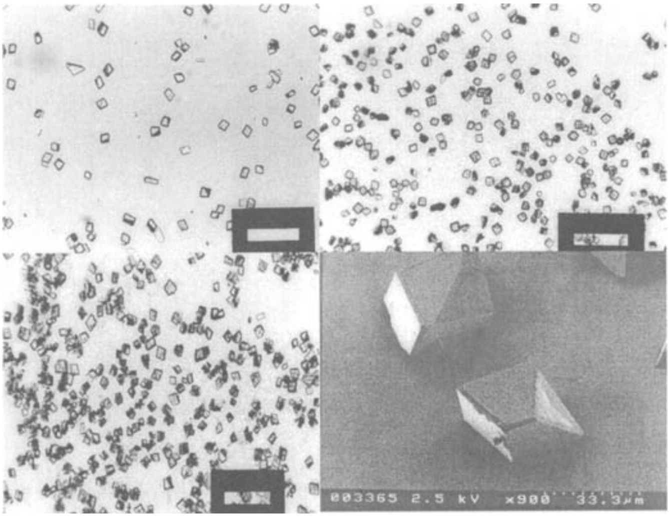

Figure 8. Illustration of effect of molecular weight on crystal growth (see text)

This result provides our second example of how control over structure and molecular weight leads to control over polymer function. The other stereo isomers of this polymer do not show the same degree of calcium carbonate crystal growth regulation.

3 A simple route to hyperbranched polymers and the influence of the structure and topology of the products on the solution properties.

Scientific and technological interest in dendrimers has grown rapidly over the last ten years or so, but bulk applications have been slow in coming and remain inhibited by the labour intensive syntheses involved. A characterising feature of dendritic polymers is that, past a critical point, their intrinsic viscosity decreases with increasing molecular weight.24) This behaviour is, of course, in marked contrast to that of the more familiar linear and lightly branched polymers and has potential technological implications. The possibility of mimicking dendritic molecular weight/viscosity behaviour in more readily accessible materials in an attractive concept.

As part of a study of AB_n hyperbranched polymers we have examined the melt polymerisation of N-acryloyl-α,ω-diaminoalkane hydrochlorides, $H_2C{=}CHCONH(CH_2)_nNH_3^+Cl^-$, (n = 2, 3, 4, 5, 6 or 7). The monomers are made by a straightforward protection/deprotection strategy and, somewhat to out surprise, they polymerised, via a Michael Addition process on heating at 210°C under nitrogen. The products, water-soluble polyelectrolytes, had the same elemental analysis as the monomers. Variation of the polymethylene spacer length (n= 2 to 7) had a marked effect on both monomer reactivity (*e.g.* n=2 reacts much faster than n=6) and the structure and properties of the polymer. The process is summarised in figure 9 for the case where n=2.

The detailed evidence justifying these assertions has been published.25) Michael addition polymerisation of these monomers can, in principle, yield secondary or tertiary amines corresponding to linear or branched sub-units. Thus amide and primary (terminal, T), secondary (linear, L) and tertiary (branched, B) amine nitrogen environments are possible. The frequency of the branched and terminal groups is connected, T = B + 1. ^{15}N Nmr spectroscopy, recorded quantitatively in natural abundance, was particularly important in making the assignment. Three signals were revealed; the amide and primary amine nitrogens were readily identified on the basis of chemical shift (relative to liquid ammonia) and literature assignments of related compounds but the signals for amine nitrogens in linear and branched units overlap; however integration allowed an assignment of the extent of branching. Thus, for polymers derived from N-acryloyl-α,ω-diaminoalkane hydrochlorides, each repeat unit contributes one amide and one amine nitrogen species. Three signals are observed in the spectra, which we assigned as one amide, and two amine salt signals. Where n=2, figure 10, the two amine salt signals are of approximately equal intensity and must represent terminal and branched units since, if the polymer was composed entirely of linear units the terminal contributions would be negligible (only one signal per chain) and the linear salt signal would be equal in intensity to the amide signal.

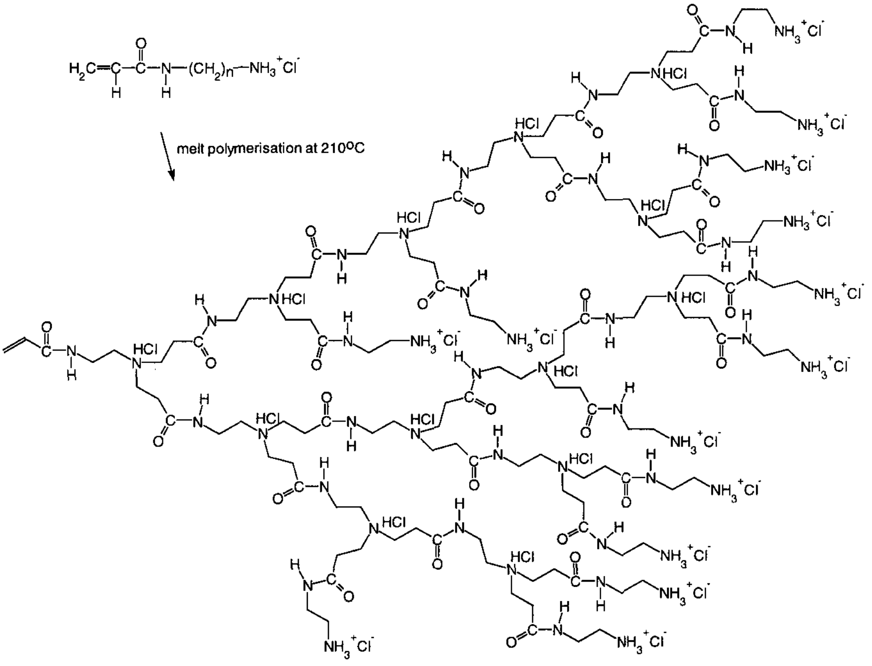

Figure 9. Structure of an AB_2 polymer hydrochloride salt, where n=2.

The fact that the sum of the relative intensities of the terminal and branched signals equals that of the amide signal means that in this case we have virtually complete branching. Increasing the internal CH_2 chain length of the monomer decreases the degree of branching; for example the polymers where n=4, display a branching factor of ~0.7, much closer to the statistical value proposed by Flory.26)

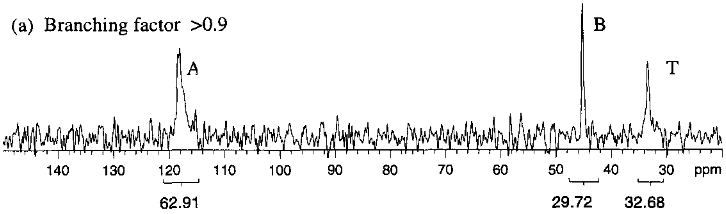

Figure 10. Quantitative ^{15}N nmr spectra (D_2O), Polymer prepared from N-acryloyl-1,2-diaminoethane hydrochloride (pH1)

These polymers display the classic polyelectrolyte viscosity/concentration behaviour, which can be suppressed by the addition of 1% lithium chloride to allow an experimental value for intrinsic viscosity to be obtained. For these polymers we observe a trend of decreasing intrinsic viscosity with increasing molecular weight, a property more associated with dendritic than with linear structure. These simple AB_2 poly(amidoamine) hyperbranched wedges are soluble in both water and methanol but are insoluble in organic solvents as their free bases. However, core terminated systems, prepared through AB_2/B_n copolymerisations using the AB_2 monomer N-acryloyl-1,2-diaminoethane hydrochloride, retain their solubility as free bases. Consequently this work provides a simple route to hyperbranched polymers with a degree of branching approaching one and some of the structural features and properties of materials with perfect dendritic architecture. Interestingly the core-terminated materials display the peak in the intrinsic viscosity vs) molecular weight normally associated with dendrimers. Thus, this third study provides another example of why precision and control in polymer synthesis can be important.

Conclusions

This paper has briefly reviewed some of the reasons why precision and control in polymer synthesis is of importance. The theme has been illustrated by describing, in necessarily brief outline, some recent results from the authors' laboratories in three areas. The theme illustrated here is quite prominent and general in present day polymer synthesis and many more examples exist, many of which were described in lectures and posters during this conference.

Acknowledgements.

This paper is a summary of the work presented by one of us (WJF) as a plenary lecture at the IUPAC World Polymer Congress in Australia in July 1998. He wishes to thank the organisers for inviting him and to acknowledge the debt of gratitude he owes to them and to the late Professor Jim O'Donnell who initially established the idea of what turned out to be a successful and dtimulating venture.

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