Star-branched polymers: 2. Linking reaction involving 2- and 4-vinyl pyridine and dienyl- and styryllithium chain ends

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The sequential copolymerization of 2- or 4-vinyl pyridine has been attempted with the aim of preparing linear triblock (ABC) copolymers. The use of either of these two monomers was found to lead to extensive, although incomplete, star-branched polymer formation. The linking reaction in this anionic polymerization of vinyl pyridine appears to be the result of the participation of the –N=CH– moiety in the pyridine ring along with the vinyl group. The addition of 4-vinyl pyridine to dicarbanionic chains in benzene or tetrahydrofuran was found to lead to both branched and crosslinked polymer. The morphology of a model star co-branch block terpolymer containing polystyrene, polyisoprene, and poly(4-vinyl pyridine) segments was examined by transmission electron microscopy.

INTRODUCTION

In recent years, some interest has been expressed[1–3] in the synthesis and properties of linear ABC triblock copolymers where A denotes polystyrene, B a polydiene and C either poly(2-vinyl pyridine) or poly(4-vinyl pyridine). Other variations have included poly(α-methylstyrene)[4] or poly(*p*-tert-butylstyrene)[5] as the third segment. The inducement for this approach is that it offers the possibility of manipulating the physical properties of a thermoplastic triblock copolymer without altering either the ratio of end segments to elastomer or the segment molecular weights. The incorporation of poly(2- or 4-vinyl pyridine) offers the further option of the additional modification of introduing an ionomer segment by the complexation of the pyridyl nitrogen with, for example, HCl[3] or nickel chloride[6].

Work in our respective laboratories involving the block copolymerization of 2- or 4-vinyl pyridine by the lithium counterion has revealed, via gel permeation chromatography, that in benzene, toluene or cyclohexane solution, as well as toluene mixed with small amounts of tetrahydrofuran, some chain linking occurs to yield star-branched material when a monofunctional initiator is used. Also branched and crosslinked material was formed when either of the two vinyl pyridines was reacted with difunctional chains involving either the lithium or sodium counterions. Our results, thus far, indicate that it is not possible to avoid this side reaction, under conventional polymerization conditions, and thus obtain only linear chains.

EXPERIMENTAL

The polymerizations were conducted either in 1 l glass reactors under vacuum or in a 4.5 l stainless steel reactor under dry nitrogen. Solvents and monomers were dried following procedures described elsewhere[7]. Toluene can lead to a chain transfer step in polymerizations involving styrene and diene monomers polymerized by alkali metal counterions[8–12]. However, under the polymerization conditions used in this work, chain transfer was found to be a negligible reaction.

n-Butyllithium or purified *sec*-butyllithium were used as the initiators for the preparation of monocarbanionic chains. Complete initiation was achieved with both organolithium species. The vinyl pyridine isomers were obtained from Croda Synthetic Chemicals Ltd and Chemical Samples. Examination of the Chemical Samples vinyl pyridines by gas and mass chromatography, after purification, failed to reveal the presence of impurities.

The 2- or 4- vinyl pyridine was added last to the polymerization reaction as a moderately dilute solution in the polymerization solvent. For the reaction at –70°C, the vinyl pyridine was distilled into the stirred contents of the reactor. Termination was carried out by the addition of methanol. Exposure of the active chains to the atmosphere was avoided since this procedure can lead to some chain coupling[13].

Polymer characterization was accomplished by gel permeation chromatography (g.p.c.). Seven 4 ft Styragel columns were used with a continuous porosity range of 10^3 to 10^6 Å. Tetrahydrofuran was the carrier solvent at 35°C. The characteristics of this 7 column arrangement have been presented elsewhere[14]. A flow rate of nearly 1 ml/min was maintained. The polystyrene calibration for this column arrangement was linear over the molecular range of 7×10^3 to 2.1×10^6 g/mol. Standard polybutadienes were also used to calibrate the column arrangement. These standards were those from these laboratories and the Goodyear Tire and Rubber Company. Solutions of about 1/4% (w/v) were used with full loop (2 ml) injections. The instrument was equipped with a 5 ml syphon and the usual refractive index detector. Duplicate runs yielded identical chromatograms for given samples.

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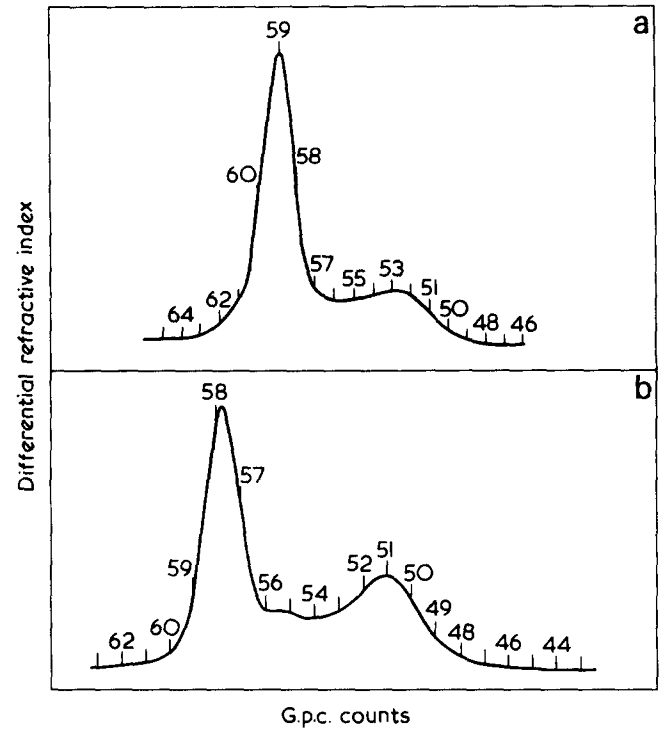

Figure 1 Gel permeation chromatograms of polybutadienes after reaction with vinyl pyridine. (a) N-110; (b) N-156

Transmission electron micrographs were obtained using the procedures and techniques described elsewhere[15,16]. The sample investigated was cast from a 9/1 (v/v) benzene/heptane mixture and annealed at 130°C for 72 h under vacuum, prior to microtoming. Staining was carried out with OsO_4 [17].

RESULTS AND DISCUSSION

The addition of both 2- and 4- vinyl pyridine to a solution of styryl-, isoprenyl- or butadienyllithium led *in all cases* to the preparation of some star-branched polymers. This branching reaction was found to occur over the temperature range 25° to 60°C. The ratio of vinyl pyridine to chain ends ranged from about 1/1 to 8/1. Higher ratios, designed to lead to poly(vinyl pyridine) segment molecular weights of 10^4 also resulted in the formation of branched polymer.

Figures 1 and *2* show chromatograms of polybutadiene and a poly(styrene–butadiene) block copolymer after reaction with either 2- or 4-vinyl pyridine. The reaction conditions and the characteristics of the linear polymer or block copolymer are shown in *Table 1*. It is apparent that extensive branching occurred in these samples (*Figures 1* and *2*). To date, conditions have not been found which allow the preparation of linear poly(vinyl pyridine) segments without the simultaneous preparation of star-branched block copolymer or terpolymer material.

We have also found that both a polyisoprene homopolymer and a poly(styrene–isoprene–styrene) block copolymer prepared by a difunctional lithium initiator[18] in benzene at 25°C showed, from g.p.c., the formation of a branched (or chain-extended fraction). A fraction of gelled material was also isolated. In these cases 4-vinyl pyridine was used. The formation of a gel fraction in these difunctional anionic polymerizations involving the vinyl pyridine isomers has been noted by other authors[19,20].

This branching–gelation process is not limited to the lithium counterion or hydrocarbon solvents. A moderately low molecular weight polystyrene ($\bar{M}_w/\bar{M}_n < 1.1$) was prepared by the use of sodium naphthalene at –70°C in tetrahydrofuran. In this case the 4-vinyl pyridine was added to the reactor by distillation, as was the styrene. Predominantly gelled material was formed. This suggests that the poly(2-vinyl pyridine) networks prepared[21] by difunctional initiation and polymerization of 2-vinyl pyridine followed by the addition of divinylbenzene were the result of the 'branching–gelation' events we have observed. Parenthetically, we should also note that we have observed that the active species involving poly(2- and 4- vinyl pyridine) with the lithium or sodium counterions fail to react with either *meta-* or *para*-divinylbenzene as was claimed elsewhere[21].

The branching (and gelation) reactions we have observed are most likely a result of the known susceptibility[22–30] of the –N=CH– unit in the pyridine ring to anionic attack. While there does not yet appear to be final agreement concerning the details of the Chitchibabin reaction[28], the general view is that the reaction proceeds by nucleophilic attack at a carbon adjacent to the nitrogen to yield either covalent or ionic structures.

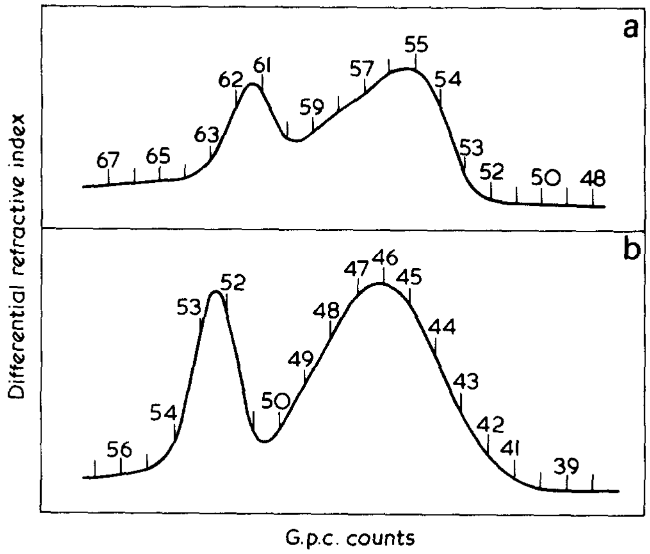

Figure 2 Gel permeation chromatograms of a polybutadiene and a poly(styrene–butadiene) block copolymer after reaction with vinyl pyridine. (a) N-173; (b) GBS-87

Table 1 Molecular characteristics and reaction conditions for chains reacted with the vinyl pyridine isomers[a]

Sample	M_n[b] 10^{-3}	Vinyl pyridine[c] Isomer	Wt %[b] Linked	$\frac{[VP]}{[RLi]}$
N-110 Polybutadiene[d]	5.0	2-VP	29	1.2
N-156 Polybutadiene[d]	4.5	4-VP	48	5
N-173 Polybutadiene	1.4	2-VP	70	5.7
GBS-87 Poly(styrene–butadiene)[e]	30	2-VP	73	8
1-Polystyrene	24	4-VP	21	5

[a] The reaction temperature was 60°C except for N-173 at 40°C and 1-polystyrene at 20°C; [b] from g.p.c. measurements; [c] for the N series the vinyl pyridine addition was continuous over the following periods; N-110 15 min, N-156 20 min, N-173 60 min; [d] tetrahydrofuran added immediately prior to the vinyl pyridine (RLi/THF = 1); [e] wt % composition of 30/70 (polystyrene/polybutadiene)

The absorption spectra of carbanions of poly(2-vinyl pyridine) show an absorption maximum at 315 nm and a shoulder between 380 and 500 nm[31–34]. This shoulder apparently corresponds to maxima between 460 and 550 nm and has been ascribed to the presence of a trienyl carbanion produced by the attack of a 'nitranion' on the vinyl group of a monomer unit. A similar spectrum was observed in this work for a polybutadienyllithium species in cyclohexane which was reacted with 2-vinyl pyridine. Spectral indications of these side reactions have also been noted by Hogen–Esch and coworkers[35,36], although they seem not to have considered the possibility of side reactions in their work. Tardi and Sigwalt[33] have outlined some of the potential side reactions that 2- and 4-vinyl pyridine can undergo in anionic polymerization systems. Although Tardi and Sigwalt[33] presented these reactions as occurring only in an intramolecular fashion, our results show that, at least for the sodium and lithium counterions, these side reactions readily occur in an intermolecular manner.

The presence of these side reactions offers a pathway by which 2- and 4-vinyl pyridine can act as 'difunctional' anionically polymerizable monomers which can lead to a star-branched polymer formation in a manner similar to that observed when divinylbenzene is added to a solution containing monofunctional carbanionic chains[15,16,37–39]. Our results thus far indicate that complete, or nearly complete linking is not possible. The maximum extent of linking observed for monofunctional chains has been about 75%. Nonetheless, the ABC triblock copolymers prepared and examined elsewhere[1–3] almost certainly, based on our findings, contained branched material and were thus not exclusively linear material as these authors[1–3] implied. It should also be noted that these reports[2–4] contained no characterization by g.p.c. which, of course, is needed in order to establish the presence or absence of branched material. Hence, the reported morphological[1,3] and physical properties[2,3] of these 'ABC' block copolymers should apparently be viewed as results obtained from triblock copolymers containing at least some non-linear chains which can be classified as pentablock (AB)$_x$C(BA)$_y$ structures with the branching occurring in the C segment. Our results indicate that the sum of x and y can range from 2 (a linear chain) to as high as 15 or more[40]. Unlike the divinylbenzene isomers, the vinyl pyridines do not lend themselves, under the conditions we have used, to the preparation of star-shaped polymers where the degree of branching can be controlled. This may be due, at least in part, to a high rate of reaction of the 'crossover' step and the subsequent steps involving the 'polymerization' of the vinyl pyridines. Our results have thus far failed to resolve the question as to whether either of the vinyl pyridine isomers can be used, as the divinylbenzene isomers have been, to prepare star-branched polymers in high yield with controlled degrees of branching.

The undisciplined characteristics of the vinyl pyridine isomers in these anionic polymerizations would seem to vitiate the kinetic studies[31,41,42] and conclusions[43] involving the homopolymerization of 2- or 4-vinyl pyridine and 2-vinyl quinoline[44]. These kinetic parameters may in reality be 'composite' copolymerization values resulting from the participation of the vinyl group and the heterocyclic ring with its attendant side reactions. The accumulated evidence would indicate that the active species present in the polymerization of vinyl pyridine include the pyridyl tight ion-pair, the trienyl carbanion and the nitranion. This latter structure could result from the direct attack of a carbanion on the pyridine ring or from resonance structures involving electron delocalization of the 2- or 4- pyridyl carbanions onto nitrogen. It is not possible, for the present, to quantify the relative contributions of these active species in the anionic crosslinking process we have observed.

The morphology of the 'ABC' block copolymers has been examined by Price[1] and Fielding-Russell[3] by transmission electron microscopy. Solvent cast films were used without an anealing step. In the case of Price[1] the elastomer segment was polyisoprene whereas polybutadiene was used by Fielding-Russell[3]. Both groups used 2-vinyl pyridine as the monomer for the C segment. There seems to be little doubt, that both groups of workers were examining block copolymers which, at least in part, contained branched material. Thus, depending on reaction conditons, the ABC materials seemingly can be a complex mixture of linear and branched material where the degree of branching can vary over a wide range of values.

We have synthesized a 'model' branched ABC block copolymer containing 4-vinyl pyridine. This sample was synthesized by linking poly(styrene–isoprene) arms by the addition of divinylbenzene (a mixture of *meta-* and *para-*isomers). The procedures for this process have been described elsewhere[15,16]. Following completion of the linking reaction, the 4-vinyl pyridine was added. The 'initiator' in this case was the polydivinylbenzene nodule which of course contained the carbon–lithium 'chain ends'. Thus, the poly(4-vinyl pyridine) chains grew out from the star polymer centre. Unlike the polymerizations involving the linear chains, the polymerization of the 4-vinyl pyridine did not lead to a noticeable change in the viscosity of the solution. This, of course, indicates that little, if any chain linking takes place in an intermolecular fashion. *Figure 3* is a chromatograph of this star-branched block terpolymer. The incorporation of the 4-vinyl pyridine (5 wt % of the block terpolymer) caused a slight shift to a lower value in the elution volume of the sample. Otherwise, the chromatograms of the samples, before and after the addition of the 4-vinyl pyridine, were identical.

It should be noted that Eschwey, Hallensleben and Burchard[45,46] were the first to exploit successfully this concept of using a polydivinylbenzene microgel nodule, containing the active 'chain ends', to initiate anionically polymerizable monomers; a procedure later used by Crossland and coworkers[47]. This procedure was also offered[48] some time ago, in a speculative fashion, as a means of preparing 'co-branched' block copolymers or terpolymers.

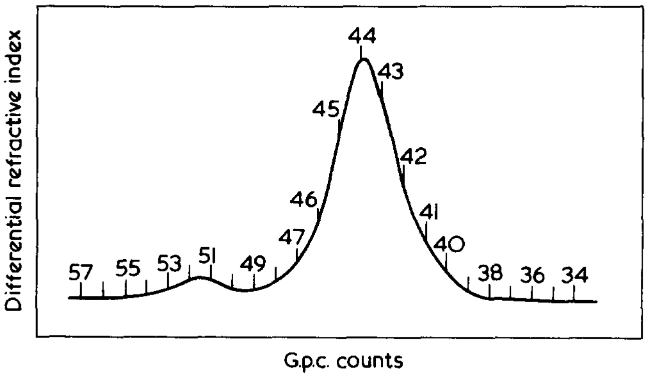

Figure 3 Gel permeation chromatogram of the (SI)$_{14}$–DVB–(4-VP) star-co-branched block copolymer. The subscript denotes the number-average number of arms.

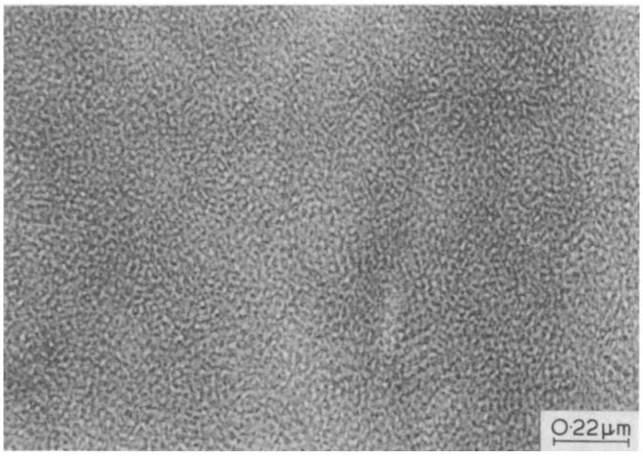

Figure 4 Electron micrograph of $(\mathrm{SI})_{14}$–DVB–(4-VP). Microtoming carried out parallel to the film surface

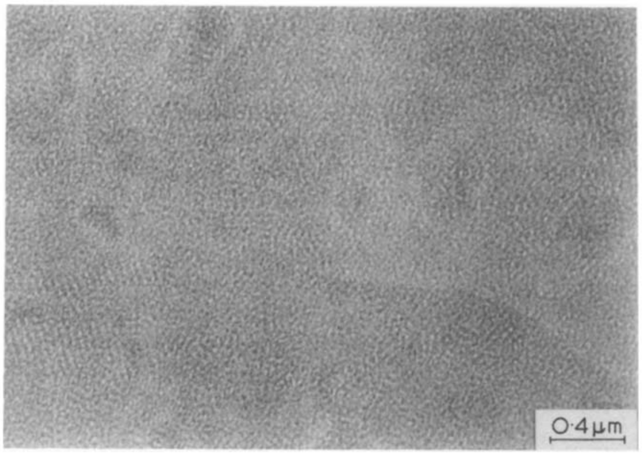

Figure 5 Electron micrograph of $(\mathrm{SI})_{14}$–DVB–(4-VP). Microtoming carried out perpendicular to the film surface

Table 2 Molecular characteristics of $(\mathrm{SI})_{14}$–DVB–(4-VP) star-co-branched block copolymer

Polymer	Composition[a] (wt %)	$\bar{M}_n \times 10^{-4}$ [b]
Polystyrene	28	1.4
Polyisoprene	66	3.4
Poly(4-vinyl pyridine)	5	
$(\mathrm{SI})_{14}$–DVB[c]		69.0
$(\mathrm{SI})_{14}$–DVB–(4-VP)		73.0

[a] Based on H-n.m.r. analysis of the SI arm and the amount of 4-vinyl pyridine added; [b] membrane osmometry in toluene at 37°C. The values presented for the star-branched materials are average from three separate $\bar{M}_n$ determinations for each sample. The estimated standard deviation was ±5%; [c] the number-average of arms is equal to 14. This value was obtained on a sample from which the unlinked SI arm was removed by fractionation.

Our morphological findings regarding this co-branched star-shaped block terpolymer are summarized in *Figures 4* and *5* while the molecular parameters are given in *Table 2*. The domain arrangements are worm-like and no significant differences could be found between specimens microtomed perpendicular or parallel to the film surface. This disordered domain arrangement is virtually identical to that observed by Price and Fielding-Russell. Their 'ABC' block terpolymers possessed overall compositions similar to our sample.

The wormlike arrangement we have seen for our star-shaped polymer is in contrast to the regular and well-defined arrangement of the polystyrene domains that we have observed[16,49] for star-branched polymers containing poly(styrene–diene) arms.

The logical comment has been offered[1,3] that as a result of the closeness of the solubility parameters δ of polystyrene ($\delta = 20.0 \times 10^{-3}\ \mathrm{J}^{1/2}\,\mathrm{m}^{-3/2}$) and the poly(vinyl pyridines) ($\delta \simeq 21.7 \times 10^{-3}\ \mathrm{J}^{1/2}\,\mathrm{m}^{-3/2}$)[50] these segments would be expected to mix and thus yield composite domains. Hence, this feature, imposed upon the novel architecture of our co-branched star-shaped block terpolymer may influence the morphology of the material. However, the fashion by which this is done is difficult to resolve, particularly so in the view of the relative position of the various segments in this branched species. Nonetheless, we have jointly noted that the addition of either vinyl pyridine isomer to the active sites of the poly(divinylbenzene) nodule of a star-branched polymer leads to the preparation of a co- or terpolymer material of reasonably well-defined architecture. This is a result of the fact that the polymerization of the vinyl pyridine at the 'protected' star centre apparently results in little, if any, interstar nuclei reactions.

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