

polymers, BB sequences would be present as —PPBBPP— and the intensity of the resonance from the PPBB tetrads would be twice the intensity of the resonance from the PBBP. This is not the case, as in *Figure 2* ref 1 the intensity of the 43.04 resonance is very nearly equal in intensity to resonance from the PBBP tetrad and not a factor of two as required. Additionally the evidence cited earlier showed that the PPBB tetrads give rise to the higher field —PB— resonance (43.3 ppm). Therefore, in view of the composition of the copolymer, the 43.04 ppm resonance in *Figure 2c* of Bunn and Cudby's paper¹ is assigned to PBPP sequences, not PPBB.

The necessary tetrad relationship⁴

$$\text{PPBB} + \text{PPBP} = \text{PPPBB} + 2\text{BPPP} \quad (3)$$

is satisfied for the spectra shown in *Figures 1–3* and *Figure 2c* in Bunn and Cudby's paper. In copolymer A (*Figure 1*) the tetrad sequences PPBB and BPPP are absent and the intensities of the 46.8 ppm and 43.3 ppm resonances are equal so:

$$\text{PPPBB} = \text{PBPP}$$

Copolymer B has no PPBP sequences and the resonance intensities are such that:

$$\text{PPBB} = \text{PPPBB} + 2\text{BPPP}$$

In the earlier discussion of *Figure 3* we showed that BPPP and PBPP ≈ 0 and that the 46.8 ppm and 43.3 ppm reso-

nances were equal so that:

$$\text{PPPBB} = \text{PPBB}$$

thus (3) is satisfied for *Figure 3*.

The spectrum in *Figure 2c* of Bunn and Cudby's paper shows no evidence for BPPP sequences. Therefore (3) reduces to:

$$\text{PPBB} + \text{PPBP} = \text{PPPBB}$$

The PPBB and PPBP tetrad sequences give a resonance at 42.76 ppm and is seen to be equal in intensity to the 46.10 ppm resonance assigned to BPPP tetrad sequences.

The assignments for —BP— centred tetrads we now propose are:

$$\left. \begin{array}{l} \text{PBPP and PPBB } 43.6 \text{ ppm} \\ \text{BBPB and PBPB } 43.6 \text{ ppm} \end{array} \right\} \text{Randall's chemical shift value}$$

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Association behaviour of poly(4-vinylbiphenyllithium) and substituted polydienyllithiums in n-hexane

M. M. F. Al-Harrah and R. N. Young

Department of Chemistry, The University, Sheffield S3 7HF, UK

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In connection with a systematic study of the anionic copolymerization of 4-vinylbiphenyl with substituted butadienes, using organolithium initiators, we required information about the degree of aggregation of the living polymers derived from these monomers. A survey of the literature revealed that the most convenient means to this end is by measurement of the viscosity of concentrated solutions which conform to the equation:

$$\eta = KM^{3.4} \quad (1)$$

in which η is the viscosity, M the molecular weight and K a constant. It has been shown that this equation is valid provided that:

$$v_2 M > 2M_e \quad (2)$$

where v_2 is the volume fraction of polymer and M_e is the molecular weight between entanglements^{1,2}.

Morton and coworkers^{3–5} devised a procedure whereby the flow time of a solution of polystyryllithium in a viscometer could be measured under high vacuum, both before and after terminating the carbanions with a trace of alcohol. Designating these flow times, respectively, as t_a and t_t , these are related to the mean degree of aggregation N of the living polymer by the equation:

$$t_a/t_t = N^{3.4} \quad (3)$$

An important extension of this procedure was developed by Morton *et al.*⁶: by 'capping' polystyryllithium by the addition of a few units of isoprene or butadiene they were able to establish unequivocally that all three of these active chain ends are virtually completely dimerized. These results have been confirmed by light-scattering studies^{6,7}.

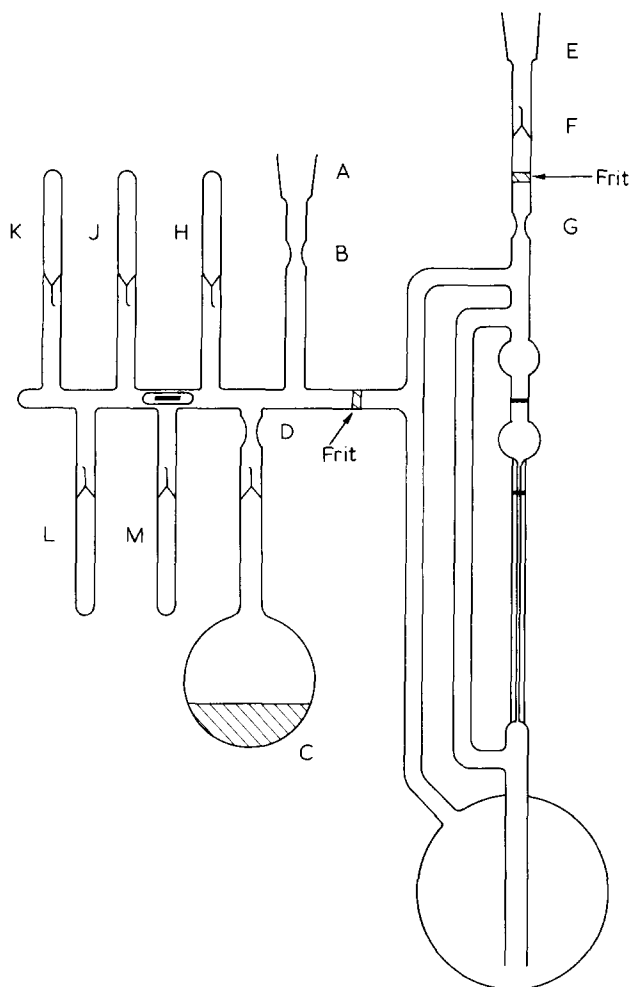


Figure 1 Vacuum viscometer used for association number measurements. Contents of ampoules: H, butyllithium in n-hexane solution; J, styrene; K, diene; L, isoprene; M, methanol. Flask C, purge solution of butyllithium in n-hexane

Experimental

4-Vinylbiphenyl was chromatographed on a column packed with alkaline alumina using n-hexane as eluent. The resulting product was sublimed twice under vacuum and then placed in ampoules.

The dienes were degassed on the high vacuum line and freed from reactive impurities by storing over a little solvent-free n-butyllithium for some 15 min. The purified materials were subdivided into ampoules.

Styrene was stored *in vacuo* over dibutylmagnesium (Lithium Corporation of America) for 1 h before being distilled into ampoules.

The viscometer which was employed is shown in Figure 1. It was attached to the high-vacuum line by socket A, evacuated and sealed-off at B. The purging solution of butyllithium in n-hexane (containing a little styrene) stored in flask C was introduced to the viscometer by shattering the intervening break-seal. The entire inner wall of the apparatus was washed with this solution. Eventually, by proper tilting of the apparatus, the purge was returned to flask C. The remainder of the apparatus was repeatedly washed by distilling solvent from C, to which the rinsings were returned. The contents of C were frozen with liquid nitrogen, and constriction D was sealed. The clean viscometer was reattached to the vacuum line by socket E, and when a satisfactory vacuum had been attained, break-seal F

was shattered with a magnetic breaker. Isoprene and n-hexane were distilled in, frozen with liquid nitrogen, then the whole assembly was removed from the line by sealing constriction G. When the reaction mixture had melted and warmed to ambient temperature, the butyllithium solution was admitted from ampoule H. The quantities of isoprene, hexane and butyllithium were chosen so as to yield a solution of polymer having values of ν_2 and M that placed it securely under the régime of equation (1). The value of M_e was taken as 7000 from the work of Fetters⁸.

Polymerization was allowed to proceed for ~10 days before the time required for the solution to flow between the fiducial marks was determined. A small quantity of styrene was introduced from ampoule J, changing the colour to yellow, and was left for a few hours to ensure com-

Table 1 Association of living lithium polymers in n-hexane at 25°C

Experiment	Anionic moiety	t_g^*/s	t_f^*/s	N
1	Isoprene	2491		1.99
	Styrene	2483		1.99
	2,3-Dimethylbutadiene	2480		1.99
	Isoprene	2500	240.0	1.99
2	Isoprene	2483		1.97
	4-Vinylbiphenyl	2463		1.97
	1,3-Pentadiene	2455		1.96
	Isoprene	2460	247.0	1.97
3	Isoprene	1896		1.96
	4-Vinylbiphenyl	1900		1.96
	2-Methyl-1,3-pentadiene	1920		1.97
	Isoprene	1890	192.0	1.96
4	Isoprene	1692		1.96
	Styrene	1606		1.93
	3-Methyl-1,3-pentadiene	1750		1.98
	Isoprene	1762	171.4	1.98
5	Isoprene	2875		1.98
	Styrene	2900		1.98
	4-Methyl-1,3-pentadiene	2690		1.94
	Isoprene	2933	281.8	1.99
6	Isoprene	1693		1.97
	Styrene	1715		1.97
	4-Methyl-1,3-pentadiene	1724		1.98
	Isoprene	1750	169.5	1.99
7	Isoprene	2385		1.96
	4-Vinylbiphenyl	2430		1.97
	2,4-Dimethyl-1,3-pentadiene	2322		1.94
	Isoprene	2500	242.0	1.99
8	Isoprene	2750		2.00
	Styrene	2700		1.99
	2,4-Hexadiene	1425		1.65
	Isoprene	2800	260.0	2.01
9	Isoprene	2200		1.98
	Styrene	2150		1.97
	2,4-Hexadiene	1139		1.63
	Isoprene	2278	215.0	2.00
10	Isoprene	2650		1.99
	Styrene	2675		1.99
	1,3-Cyclohexadiene	1590		1.71
	Isoprene	2825	255.5	2.03
11	Isoprene	2354		1.94
	Styrene	2405		1.95
	1,3-Cyclohexadiene	1493		1.69
	Isoprene	2429	248.6	1.94

* Each time listed is the average of six observations

Table 2 Summary of results of association measurements

Anionic moiety	\bar{N}	Number of independent observations
Isoprene	1.97	11
Styrene	1.97	8
4-Vinylbiphenyl	1.97	4
2,3-Dimethylbutadiene	1.99	1
1,3-Pentadiene	1.96	1
2-Methyl-1,3-pentadiene	1.97	1
3-Methyl-1,3-pentadiene	1.98	1
4-Methyl-1,3-pentadiene	1.96	2
2,4-Dimethyl-1,3-pentadiene	1.94	1
2,4-Hexadiene	1.64	2
1,3-Cyclohexadiene	1.70	2

plete reaction and the flow time was redetermined. A substituted diene (0.1 cm^3) was added from K, rapidly discharging the colour. Again, a few hours were allowed to elapse before the new flow time was determined. Isoprene ($\sim 0.2 \text{ cm}^3$) was now introduced from L to convert the chain ends to their original constitution, so enabling a check on whether any significant destruction of carbanions had been occasioned by the several additions of reagents. Finally, 0.1 cm^3 of degassed methanol was added from M and the flow time of the terminated polymer was obtained. The results of those few experiments in which the flow time of the polymer finally capped with isoprene was significantly different from the starting flow time were rejected. The results which were deemed satisfactory are shown in Table 1, and summarized in Table 2.

In agreement with previously published work³⁻⁷, polystyryllithium and polyisoprenyllithium were found to be almost completely associated as dimers. Poly(4-vinylbiphenyllithium), together with the polydienyllithiums derived from 2,3-dimethylbutadiene, 1,3-pentadiene, from

2-, 3- and 4- methylpentadienes and from 2,4-dimethylpentadiene (none of which seem to have been studied before) also prove to be almost completely dimerized. However, poly(2,4-hexadienyllithium) and polycyclohexadienyllithium are markedly less strongly associated, having mean degrees of aggregation of 1.64 and 1.70, respectively. Morton *et al.* have reported⁹ a mean value of 1.37 for poly(2,4-hexadienyllithium) in benzene and hexane, and suggested that the low degree of association might be due either to steric restrictions prevailing in secondary carbanions or to the greater ionic character revealed by the n.m.r. spectrum. Similar logic could be applied to polycyclohexadienyllithium. The cause of the difference between our value of N for polyhexadienyllithium and that reported by Morton *et al.* is obscure since similar organolithium concentrations ($\sim 3 \times 10^{-3} \text{ M}$) were employed by both groups of investigators.

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