A viscometric study of the interaction of polybutadienyllithium with N,N,N',N'-tetramethylethylenediamine in benzene[†]

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Moderately concentrated solutions of polystyryllithium in benzene were prepared under high vacuum conditions in an Ubbelohde viscometer and the active chain ends were 'capped' with a few molecules of butadiene. The flow times of these solutions were determined before and after the addition of small aliquots of N,N,N',N'-tetramethylethylenediamine (TMEDA) and finally following protonation of the carbanions with a trace of alcohol. The addition of the TMEDA caused a decrease in the viscosity that was slightly greater than that predicted on the basis that two molecules of TMEDA cause the disaggregation of a dimeric polybutadienyllithium associate.

Keywords Butadiene; polybutadienyllithium; viscosity; N,N,N',N'-tetramethylethylenediamine; association; anionic polymerization

INTRODUCTION

Interest in the influence of TMEDA upon the course of anionic polymerization was originally largely due to the observation by Langer[1] that the lethargic polymerization of ethylene by butyllithium becomes a very much more rapid process in the presence of TMEDA and leads to the formation of products of quite high molecular weight. Several groups have studied the influence of TMEDA upon the polymerization of butadiene and some of its derivatives but have obtained results that are apparently contradictory. Hay and McCabe reported[2] that the reactivity of butyllithium towards butadiene is greatly increased by TMEDA; initiation by the 1:1 complex with butyllithium is rapid and propagation is by the loose ion pair of stoichiometry BdLi:2TMEDA. Davidjan *et al.*[3] found that the presence of TMEDA causes a significant increase in the rate of polymerization of isoprene by butyllithium, a plateau being reached at a ratio of base:lithium $\simeq 4$. The same group, however, found[4] that TMEDA causes a decrease in the propagation rate of poly(2,3-dimethylbutadienyllithium). Dumas *et al.*[5] observed a decrease in the rate of propagation of polyisoprenyllithium, reaching a lower limit at base:lithium ratios of $\gtrsim 0.5$. Extension of their work revealed[6] that an increase or a decrease in the rate of polymerization of isoprenyllithium may be observed, depending upon the absolute concentration of organolithium compound. This same phenomenon has been described in the case of polystyryllithium propagation by Helary and Fontanille[7] who noted that, since propagation is first order in stryryllithium in the presence of

TMEDA but one-half order in its absence, the corresponding straight lines in a plot of ln(rate) vs. ln[RLi] necessarily intersect. For [RLi] greater than that corresponding to this intersection, the rate is increased by the presence of TMEDA, and vice versa.

Fractional kinetic orders are generally observed in systems where there is association of organolithium species. In the case of styrene, the propagation rate[8] is proportional to the square root of the total organolithium concentration and carbanionic chain ends are virtually entirely dimerically associated[9-13]. The change to a first-order dependence in the presence of TMEDA presumably implies destruction of this dimeric aggregation. Fractional orders, in the range one-quarter to one-sixth, are generally reported for the propagation of polydienyllithium species[14-16]. Most investigations have concluded that these species are dimerically associated[9-12,18-22], although one group claims tetrameric association[13]; a simple inverse relationship between the multiplicity of the aggregation and the kinetic order would not therefore appear to be a general phenomenon.

The presumption that TMEDA disrupts the aggregation of polymers bearing an organolithium end group is entirely reasonable but lacks direct supporting experimental evidence. The present work was intended to remedy this situation in the case of polybutadienyllithium. It has been shown[10-12,18,19] that the association states of such polymers in pure hydrocarbon solvents can be determined by the application of the relationship for the viscosity of concentrated solutions:

$$\eta = K\bar{M}_w^{3.4} \tag{1}$$

where η is the viscosity, $\bar{M}_w$ is the weight-average

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Table 1   G.p.c. analysis of terminated polymers

Sample	$10^{-5} M_n$	$10^{-5} M_w$	$10^{-5} M_z$
10	2.14	2.17	2.31
12	2.38	2.50	2.67
13	2.40	2.50	2.65

Table 2   Influence of TMEDA upon the weight-average degree of association (N_w) of polybutadienyllithium in benzene

$\dfrac{[TMEDA]}{[RLi]}$	Mean flow time (s)	Number of observations	Standard deviation(s)	N_w
Experiment 10 (27.1°C), volume fraction of polymer ~0.18				
0	1596.5	4	2.2	2.00
0.118	1134.8	6	11.1	1.80
0.298	725.8	5	2.1	1.58
0.586	381.5	6	2.5	1.31
terminated	152.2	6	0.2	
Experiment 12 (28.6°C), volume fraction of polymer ~0.20				
0	4248	4	14.5	2.02
0.166	2522.6	5	24.2	1.74
0.569	891.5	5	3.4	1.28
1.13	420.0	4	0.7	1.02
terminated	386.6	4	1.8	
Experiment 13 (28.6°C), volume fraction of polymer ~0.20				
0	3665.3	4	21.3	1.99
0.229	1867.7	5	19.7	1.63
0.576	572.5	6	3.5	1.15
1.10	365.7	4	0.4	1.01
terminated	350.9	4	0.7	

molecular weight and K is a constant. This equation is valid[23,24] provided that

$$\phi_2 \bar{M}_w > 2M_c \qquad (2)$$

where ϕ_2 is the volume fraction of polymer and M_c is the molecular weight between entanglements. In practice, equation (1) may be conveniently re-expressed as:

$$t_a/t_t = (\bar{M}_a/\bar{M}_t)^{3.4} = N_w^{3.4} \qquad (3)$$

where t_a and t_t denote the flow times of the active and terminated solutions, $\bar{M}_a$ and $\bar{M}_t$ the molecular weights of the active and terminated polymers, and N_w is the weight-average degree of association.

EXPERIMENTAL

Benzene was stirred over concentrated sulphuric acid for a week, decanted and repeatedly washed with water. Drying was achieved by treatment with calcium hydride followed by sodium–potassium alloy.

TMEDA was refluxed over molten potassium for 2 h and distilled into a flask containing sodium–potassium alloy. Analysis of the product by v.p.c. showed that the only detectable impurity was ~0.6% trimethylethylenediamine which was deemed insignificant for the purposes of the present work. A stock solution in benzene (~0.4 M) was prepared under high vacuum conditions and subdivided into capillary ampoules (~0.05 cm³ solution) fitted with breakseals.

Butadiene was purified by purging out impurities with solvent-free n-butyllithium: the monomer was recovered

after a short period by distillation.

sec-Butyllithium was prepared in the usual way from *sec*-butylchloride and excess lithium dispersion in n-hexane. The solvent was removed from the filtered solution and the crude butyllithium was distilled under high vacuum; the pure product was dissolved in n-hexane and distributed into ampoules fitted with breakseals.

Styrene was dried by storage over calcium hydride. Residual impurities were purged by standing over solvent-free dibutylmagnesium; the pure product was recovered by distillation.

Polybutadienyllithium and polystyryllithium solutions were prepared under rigorous high vacuum conditions using a large Ubbelohde viscometer in the manner described previously[19]. The viscometer was maintained at constant temperature by submersion in a large water-filled thermostat.

G.p.c. analysis of the terminated polymers was conducted using a Waters Ana-Prep instrument with seven 4 ft Styragel columns having porosities ranging from 2 × 10³ to 5 × 10⁶.

RESULTS

An initial experiment was conducted using a 30% (v/v) solution in n-hexane of polybutadienyllithium of 43 000 molecular weight—a composition securely in the domain of applicability of equation (1)[9]. However, the flow time was in excess of 10 h—unacceptably long for experiments in which it is necessary to determine the average of several successive determinations. A much more serious problem was revealed by the observation that the flow time slowly increased with increasing sample age. There are two obvious possible causes: (a) incomplete polymerization at the time of the first measurement and (b) progressive crosslinking of chains as a consequence of the attack of the anionic end of one chain upon an olefinic moiety (backbone or pendant vinyl) in another. Possibility (a) was rejected on the grounds that the viscosity was still increasing after three days; the likelihood of possibility (b) was fortified by the observation of gelling of polybutadienyllithium reported by Morton and Fetters[9]. This problem was solved by the simple expedient of preparing polystyryllithium of appropriately high molecular weight and converting its anionic chain end to butadienyllithium by the addition of a very small amount of butadiene monomer. There was no evidence for any change in the flow time of such a solution over the period required for the experiments reported in the present work. In calculating suitable combinations of polystyrene molecular weight and volume fraction a value of M_c of 18 000 was adopted[18,24]. G.p.c. analysis (*Table 1*) showed that the samples had sharp distributions.

The volumes of the aliquots of TMEDA solutions added to the viscometer were kept as small as was practicable, viz. ~0.05 cm³. In general, the viscosities of concentrated solutions are acutely sensitive to dilution: by way of illustration, η for polystyrene in butylbenzene[25,26] is proportional to (concentration)[7.5]. For the same reason, the total number of successive additions of TMEDA solutions was limited to three: the maximum total dilution was 0.2%. The resulting data, shown in *Table 2*, are the average values of (usually) six successive determinations of flow time. The scatter of flow times was small: altering the mean flow times by their standard deviations altered the calculated N_w by ±0.005 or less, all

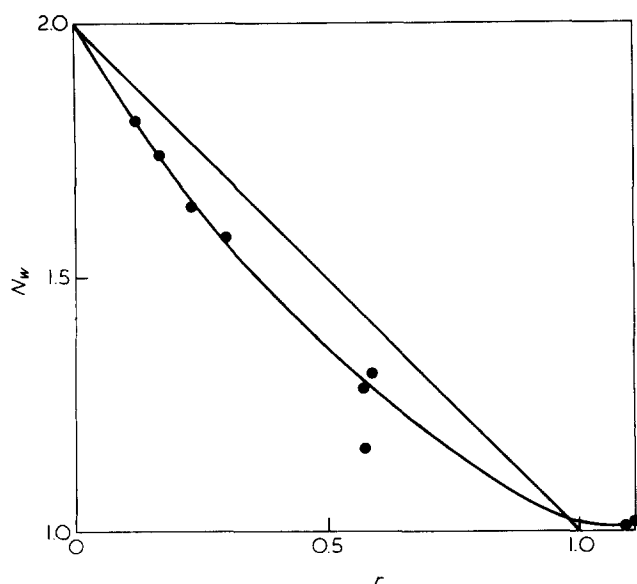*Figure 1* The dependence of the weight-average degree of assocation (N_w) upon the [TMEDA]:[Li] ratio (r)

calculations of N_w being based on the ratio of the flow times of active and terminated solutions.

A smooth curve can be drawn (*Figure 1*) passing through, or close to, all the points, with a single exception.

The value of N_w for all three polymer solutions prior to the addition of TMEDA was almost exactly 2, in accordance with earlier observations and corresponding to a dimeric association of the butadienyllithium chain ends. The addition of TMEDA causes a sharp drop in N_w. If it is assumed that two molecules of TMEDA can completely complex and dissociate one dimer according to the scheme

$$(Bd_nLi)_2 + 2TMEDA \rightarrow 2Bd_nLi.TMEDA \qquad (4)$$
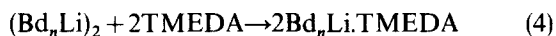
then the weight-average molecular weight ($\bar{M}_w$) can readily be calculated. If the ratio [TMEDA]:[Li] is designated r, and the molecular weight of a non-aggregated polymer M_1, then

$$\bar{M}_w = \frac{(2M_1)^2(1-r)/2 + M_1^2 r}{2M(1-r)/2 + M_1 r} = M_1(2-r) \qquad (5)$$

and the weight-average degree of aggregation

$$N_w = 2 - r \qquad (6)$$

The line corresponding to this linear dependence of N_w upon r is shown in *Figure 1*. It is at once evident that N_w falls somewhat faster than this line predicts. Plainly, rewriting (4) as an equilibrium cannot provide an explanation since this would cause N_w to fall more slowly than the straight line indicates. There are several possible explanations of the observed behaviour:

(a) impurity in TMEDA destroys some carbanions,
(b) occurrence of chain metallation,
(c) occurrence of TMEDA metallation,
(d) formation of cyclopentyllithium,
(e) change of carbanion conformation,
(f) change in mean lifetime of dimers.

If it is assumed that one molecule of impurity terminates one carbanion, comparison of the observed N_w with that calculated for a pure system conforming to (4) would imply that at low r (~ 0.1) the concentration of impurity is almost equal to that of the TMEDA. In addition, the level of impurity would have to decrease with increasing r (*Figure 1*). Since v.p.c. failed to detect any significant impurity, and since ampoules were filled using a master reservoir, suggestion (a) can be discounted.

Suggestion (b), that one chain may metallate another, so creating both uncharged and multiply charged chains, and suggestion (c) may both be eliminated from further consideration on the grounds that flow times did not change with time. It is inconceivable that such metallations could proceed to a state of equilibrium within the time of first mixing.

It has been established[27] that in the presence of TMEDA the carbanionic chain end of polybutadieneyllithium can attack a penultimate pendant vinyl group:
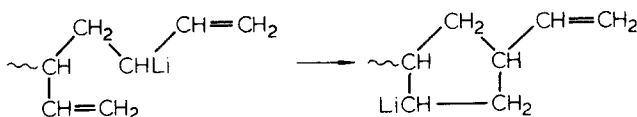
Under the conditions of temperature and concentration employed in capping the polystyryllithium only some 7% of the chains might possess the necessary penultimate vinyl placement[28]. Furthermore, if an analogy can be drawn with alkyllithium species such as *sec-* or *tert-*butyllithium, it might be anticipated that such a cyclopentyllithium might be tetramerically associated. Clearly, suggestion (d) is incapable of explaining the actual observations.

The conformation of the carbanionic moiety in polybutadienyllithium is known to be $\sim 75\%$ *trans* in hydrocarbons[21] but $\sim 34\%$ *trans* in THF at $0°C$.[13] It is conceivable that the different steric interactions might result in differing degrees of aggregation of polybutadienyllithium having differing carbanionic conformations. A study of the ^1H n.m.r. spectra of oligomeric 1,1,3,4-d_4-butadienyllithium showed[29] that the effect of TMEDA upon conformation is much too small to account for the viscometric behaviour and so (e) can also be eliminated from further consideration.

In a concentrated solution, the chains are constantly tangling and disentangling by diffusion. In the case of a dimeric associate held together by labile central bond, disentanglement may also proceed by dissociation followed by reassociation, or by exchange involving pairs of aggregates. Worsfold has suggested[30] that, if the mean lifetime of association is much smaller than that of an entanglement, the concentrated solution viscosity will approach that of the unassociated polymer. If this is indeed the case, it may provide an explanation of the present results in terms of the further exchange

$$(Bd_n^*Li.TMEDA) + (Bd_nLi)_2 \rightleftharpoons (Bd_nLi.TMEDA) + (Bd_n^*Li.Bd_nLi)$$
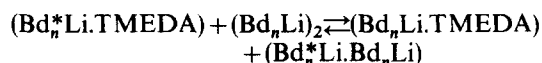
Unfortunately, Worsfold's proposal is purely qualitative and a quantitative test must await the development of suitable theory.

ACKNOWLEDGEMENTS

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