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STEREOCHEMICAL CONTROL IN ANIONIC POLYMERIZATION OF 2-VINYLPYRIDINE AND RELATED VINYL MONOMERS

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The alkylation, silylation and other electrophilic reactions of 1-lithio-1,3-bis(2-pyridyl)butane (2a) in THF at −78 °C leads to *meso*-like products that may be accounted for by intramolecular coordination of Li ion with the penultimate 2-pyridyl group. This is also demonstrated by proton-transfer equilibria between 1-lithio-2-ethylpyridine and 2a, allowing the determination of the ΔH and ΔS of intramolecular chelation in 2a. The ΔS of chelation is nearly zero, probably as a result of chelation-induced desolvation of Li ion. Surprisingly, however, the corresponding addition of 2-vinylpyridine to 2a and higher P2VPLi homologs in THF is not stereoselective. In toluene at −78 °C the t-BuLi-initiated polymerization of 2-VP is actually somewhat syndiotactic ($rr = 0{\cdot}44$). The presence in this polymerization of at least one equivalent of t-BuOLi or other tertiary ROLi surprisingly leads to isotactic P2VP. SEC viscometric and other studies indicate that both the P2VPLi– and P2VPLi–ROLi complexes are monomeric in toluene. The stereochemistry is apparently due to a 1:1 P2VPLi–ROLi complex that discriminates between the two pro-chiral faces of the anion by preferential coordination of the ($ROLi_2$) moiety to the *meso*-prochiral face. Isotactic-like addition now occurs by electrophilic attack of 2-VP that is *syn* with respect to the ($ROLi_2$) 'counter ion.'

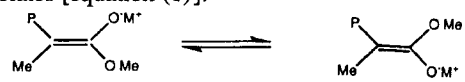
INTRODUCTION

Isotactic control in the anionic polymerization of MMA was first achieved in the late-1950s in apolar solvents (toluene, hexanes) and in the presence of small counter ions.[1–8] Typical initiator systems included n-BuLi–toluene at −78 °C, Grignards in cyclohexane or toluene at −78 °C. The degree of isotactic control in some of these systems is typically high. The formation of monodisperse highly isotactic (96%) PMMA has recently been demonstrated by Hatada *et al.*[9]

On the other hand, the presence of donor solvents such as diethyl ether (DEE), THF and DME leads to a sharply decreased isotactic content depending on the concentration of the donor solvent. In pure THF at −78 °C polymerization of MMA in the presence of Li ion gives rise to predominantly syndiotactic PMMA ($rr = 0{\cdot}70$–$0{\cdot}80$).[8]

Almost from the beginning, isotactic control in the MMA polymerization was ascribed to interactions of the Li counter ion with the carbonyl of the penultimate ester groups. Examples due to Cram and Kopecky[10] and Fowells *et al.*[2] are shown in Scheme 1.

Owing to a lack of comparable systems for other monomers, such descriptions of necessity were *ad hoc* and qualitative. Furthermore, rationalization of stereochemical control is restricted, or should be, to cases of rather pronounced tactic control. For instance, an isotactic content of 80% at −78 °C requires a transition-state free energy difference of about 0·9 kcal (1 kcal = 4·184 kJ) between *meso* and racemic additions. Differences less than that are not readily interpretable, particularly in view of the complexities involved in the addition process. These complexities pertain both to the propagating chain and to the monomer itself. Thus, the chain-end carbanion in the case of MMA is strongly resonance stabilized and thus exists as two possible stereoisomeric (*E*)- and (*Z*)-enolates [equation (1)].[10–12]



(1)

Furthermore, since the carbanion is pro-chiral and since anionic polymerization of MMA and analogous monomers such as 2-vinylpyridine (2VP) in media such as THF, DEE and toluene generally involves tight ion pairs, the counter ions may be present at either of the pro-chiral faces of the carbanion (Scheme 2). Such faces may be termed pro-*m* or pro-*r* when covalent bond formation occurring at that face generates a *meso* or racemic dyad, respectively (Scheme 2).

Thus M^+ side (*syn*) electrophilic attack by monomer or other electrophile (EX) on the pro-*m* face would give rise to a *meso* or *meso*-like dyad. The preference of the cation that may be complexed by a solvent or ligand L for one of the two pro-chiral faces together with the mode of monomer attack (*syn* or *anti*) would co-determine the stereochemistry. Intramolecular chelation

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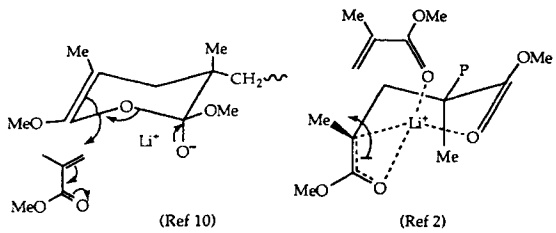
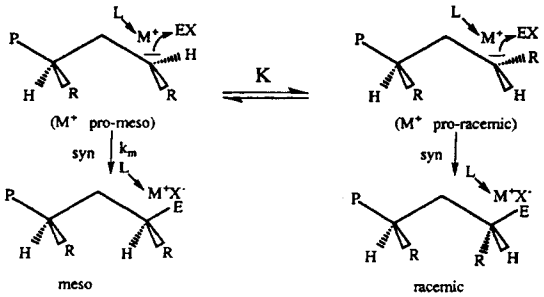


Scheme 1. Proposed mechanisms accounting for isotactic anionic polymerization of MMA in non-polar media



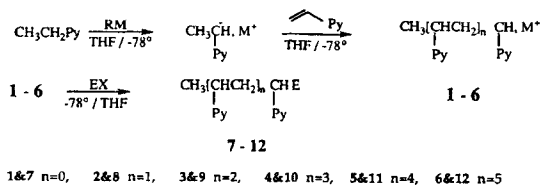
Scheme 2. Diastereomeric pro-chiral ion pairs in anionic vinyl polymerization

of M^+ by the penultimate R group could be just one of the mechanisms by which one of the ion pair diastereoisomers is favored.

In the following, we report some recent studies on the mechanisms of stereocontrol related to Scheme 2.

RESULTS AND DISCUSSION

Earlier work had centered on the stereochemistry of anionic oligomerization of 2-vinylpyridine [equation (2)].[13–16]



(2)

These studies were undertaken since, in contrast to the ester enolate anions, the pyridine-substituted anions are far less prone to side-reactions at elevated temperatures. Furthermore, the position of the nitrogen in the ring may be varied providing additional leverage on the interpretation of mechanistic aspects (see below).

Anions **1–6** in non-polar solvents and even in moderately polar solvents such as THF exist predominantly as ion pairs. Table 1 gives dissociation constants in THF of 1-phenyl-1-(2-pyridyl)- (**13**) and 1-phenyl-1-(4-pyridyl)- (**14**) substituted anions along with the corresponding 1,1-diphenyl analog anions (**15**). The introduction of a nitrogen atom in the 2- or 4-position in the ring leads to decreases of the order of $10–10^2$ in the dissociation constants.

The dissociation constant of the less delocalized picolyl anions (**16**) is even lower. The stability of ion pairs of 2- or 4-pyridine-substituted anions relative to the free anions is clearly due to enhanced electron density at the heteroatom. This is illustrated by the higher dissociation constant of the 1-phenyl-1-(3-pyridyl)-substitution anion.[17] In this case, resonance delocalization of negative charge on to the nitrogen is not possible. Similar low dissociation constants in THF have been reported for enolates such as the PMMA anion lithium salt (Table 1).[20,21]

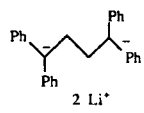
The stereochemistry of methylation (CH_3I) at −78 °C in THF as a function of cation size and coordination is summarized in Table 2. The degree of methylation stereoselectivity is very high (>99% *meso*) in the case of Li ion but decreases sharply for larger cations or in the presence of strongly cation-coordinating agents.[13–15] This result was rationalized by the occurrence of strong intramolecular cation coordination of Li or Na by the penultimate 2-pyridine group (Scheme 3).

The pro-*meso* form of **2** is favored over the diastereomeric pro-racemic **2** by virtue of a *gauche* interaction between the PCH_2 and the CH_2C^- bond in pro-racemic **2**. Molecular models show additional non-bonded interactions in pro-racemic **2** between the THF-coordinated Li ion and the penultimate asymmetric center that could amount to ≥ 1 kcal mol^{-1}. As a result, the predominant *meso* stereochemistry is consistent with a *syn* attack of CH_3I on the pro-*meso* ion pair (Scheme 3).

The results in Table 2 are consistent with the above important role of intramolecular cation coordination. First, intramolecular ion–dipole interaction is expected to decrease with increasing cation size and cation coordination (Table 2). Thus, methylation stereoselectivity for the Cs and cryptated (2.1.1) lithium derivatives decreases to 65 and 50% *meso*, respectively. Further, replacing the penultimate group with phenyl results in an essentially complete lack of methylation stereoselectivity. Careful inspection of Scheme 3 and of space-filling models show that the presence of 3′-methyl-2-pyridine as a penultimate group ($R^1 = Me$, $R^2 = H$) would lead to *peri* non-bonded interactions between the 3′- and equatorial methyl groups and would eliminate methylationstereoselectivity, whereas that for the dimer anion having a 5′-methyl-2-pyridine group ($R^1 = H$, $R^2 = Me$) the stereoselectivity would not be affected. These predictions were fully confirmed (Table 2).[16] Scheme 3 also predicts that for the Li salts of trimer, tetramer and highly oligomeric anions the stereoselectivity would remain high. This also was confirmed.[22]

Quantitative data on the extent of intramolecular

Table 1. Dissociation constants of lithium salts of phenyl-, 2- and 4-pyridyl- and ester-stabilized anions in THF at −78 °C



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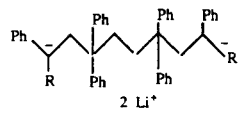
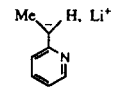


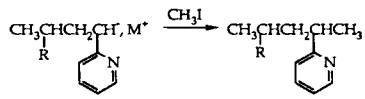
13 R = -2-pyridyl
14 R = -4-pyridyl



16

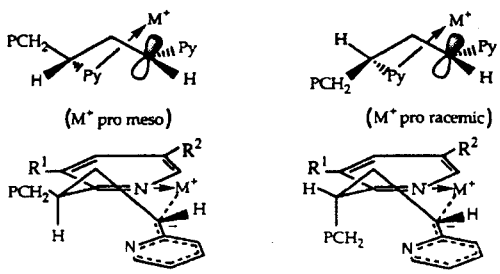
	Anion						
	15	**13**	**14**	**16** (Na^+)	**16**	PMMĀ Li^+	PMMĀ Li^+
10^9 *K* d (M)	4000	280	60	0·14	3·1	0·40	10^{-2}–10^{-4}
Ref.	17	17	17	18	19	20	21

Table 2. Methylation stereochemistry of alkali metal salts of various dimer anions at −78 °C in THF as a function of penultimate group, cation and cation coordination



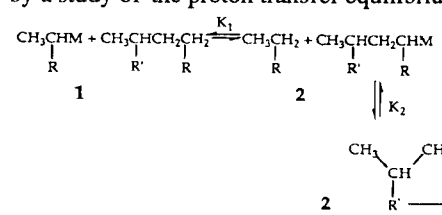
R	M^+	Fraction 2*R*,4*S*/2*S*,4*R*	R	M^+	Fraction 2*R*,4*S*/2*S*,4*R*
2-Pyridyl	Li	0·99	2-Pyridyl	Epim.[a]	0·49
2-Pyridyl	Na	0·95	Phenyl	Li	0·50
2-Pyridyl	K	0·85	3′-Methyl-2-pyridyl	Li	0·24
2-Pyridyl	Rb	0·76	5′-Methyl-2-pyridyl	Li	0·98
2-Pyridyl	(Li, 2.1.1)[d]	0·65	4-Pyridyl[b]	Li	0·69
2-Pyridyl	(Na, 2.2.2)[d]	0·58	2-Pyridyl[c]	Li	0·50

[a] Epimerization conditions: *meso*-isomer in t-BuOK–DMSO at 25 °C for 100 h.
[b] 1,3-Bis(4-pyridyl) butane anion.
[c] 1-(4-pyridyl)-3-(2-pyridyl) butane anion lithium salt.
[d] Cryptates.



Scheme 3. Intramolecular coordination as a factor in the anionic polymerization of 2-vinylpyridine

coordination of the Li salt of **2** in THF were obtained by a study of the proton transfer equilibrium (3).[23]



a R = R' = -2-pyridyl. b R = 2-pyridyl, R' = phenyl. c R = -2-pyridyl, R' = 3'-methyl-2-pyridyl.

(3)

Table 3. Chelation equilibrium constants K_2 in equation (3) in THF as a function of penultimate group R′, counter ion and temperature

R′[a]	M^+	Temperature (°C)	K_2	R′[a]	M^+	Temperature (°C)	K_2
2-Py	Li	25	15·2	2-Py	Na	25	2·3
Ph	Li	25	0·8	2-Py	Na	0	3·0
3′M2Py	Li	25	1·0	2-Py	Na	−25	3·7
2-Py	(Li, 2.1.1)[b]	25	1·2	2-Py	Na	−35	4·1
2-Py	Li	0	20·0	2-Py	(Na, 2.2.1)[b]	25	1·8
2-Py	Li	−12	21·6	2-Py	K	25	1·8
2-Py	Li	−25	25·3	2-Py	K	0	1·9
2-Py	Li	−35	28·7	2-Py	K	−25	2·1
2-Py	(Li, 2.1.1)[b]	−25	1·5	Ph	K	25	0·3

[a] 2-Py = 2-pyridyl, Ph = phenyl, 3′M2Py = 3′-methyl-2-pyridyl.

Table 4. Thermodynamic parameters for intramolecular cation coordination (K_2) for Li, Na, and K salts of 1,3-bis(2-pyridyl)butane anion (**2a**) in THF

M^+	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} K^{-1})
Li	−1·4 (±0·10)	0·80 (±0·4)
Na	−1·3 (±0·15)	−2·60 (±1·0)
K	−0·5 (±0·20)	−0·40 (±1·2)

Methylation (CH_3I) of the equilibrium mixture is rapid (*ca* 1 s) compared with the proton transfer reactions (>24 h), so that GC analysis readily gives apparent equilibrium constants (Tables 3 and 4). The overall reaction may be written as the sum of two steps, the first (K_1) being the proton transfer leading to a dimer anion in which the intramolecular coordination of M^+ by penultimate pyridine is absent and the second step being the intramolecular chelation (K_2).

The overall equilibrium of equation (3) is written as

$$K = K_1(1 + K_2) \tag{4}$$

Assuming that the stabilities of anions **1** and the unchelated **2** are identical, K_1 becomes unity, so that

$$K_2 = K - 1 \tag{5}$$

Table 3 shows the values of K_2 for Li, Na and K salts of **2a** and for analogs **2b–2d** having phenyl 3′-methyl-2-pyridyl and 5′-methyl-2-pyridyl as penultimate groups. Clearly, the K_2 values decrease with increasing cation radius and with substitution of penultimate pyridine with groups incapable of strong cation coordination such as phenyl and 3′-methyl-2-pyridine (see also Table 2).

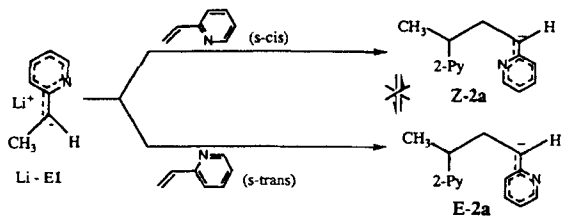
The temperature dependence of equilibrium (3) for Li, Na and K salts of **2a** gave the ΔH and ΔS values of intramolecular cation coordination (Table 4). The ΔH values give a predictable decrease in the enthalpy as the cation radius increases. Interestingly, the ΔS value of intramolecular coordination is low. Apparently, this is because intramolecular coordination of the metal ion liberates an M^+-coordinated THF, thus offsetting a loss of entropy incurred in the intramolecular coordination.

The above unambiguously demonstrates the intramolecular coordination in anions **2a**. There is ample reason to assume that the same process occurs in all oligomer and polymer anions since methylation ster-

Table 5. Stereochemistry of reaction of various electrophiles with the Li salt of dimer anion **2a** in THF at −78 °C

EX	Fraction 2*R*,4*S*/2*S*,4*R*	EX	Fraction 2*R*,4*S*/2*S*,4*R*
CH_3I	0·99	Me_3SiCl	0·97
CH_3Br	0·98	$CH_2{=}C(Ph)_2$	0·93
CH_3Cl	0·98	$CH_2{=}C(Ph)_2$[a]	0·63
C_2H_5I	0·97	$(CD_3)_2CO$	0·85
i-C_3H_7Br	0·95	PhCHO	0·71
$PhCH_2Cl$	0·97	4-VP	0·97
Ph_2CHCl	0·96	2-VP	0·64

[a] At 25 °C.



Scheme 4. *s-cis* and *s-trans* addition of 2-vinylpyridine to 1′-lithio-2-ethylpyridine in THF at −78 °C

eochemistry in the presence of Li or Na ion remains highly *meso* selective for all degrees of polymerization (>96% *meso*).[22]

Table 5 shows the stereochemistry for several other reactions of **2a** including alkylations with other groups such as ethyl, isopropyl and benzyl.[24] Also included are reactions with Me_3SiCl, $(CH_3)_2CO$, diphenylethylene and 2- and 4-vinylpyridine. All of these reactions show predominant formation of the same *meso*-like products. However, the stereoselectivity, especially in the case of 2-vinylpyridine, is very low and indeed the stereochemistry of poly(2-vinylpyridine) under these conditions is essentially atactic with minimal isotactic preference (*mm* = 0·45).[25–27] The reason(s) for this remarkable lack of stereoregularity is not clear, but it could be due to the requirement for intramolecular coordination of Li ion in the newly formed anion. Furthermore, the approach of the 2-VP monomer to the 1′-lithio-2-ethylpyridine lacks stereoselectivity since both *E*- and *Z*-isomers are formed in approximately equimolar amounts (Scheme 4).[28,29] It is probable that this lack of stereoselectivity is related to the mode of 2-VP presentation to the Li salt of **1** since *E*–*Z* interconversion was shown to be slow on the reaction time-scale. Thus, *s-cis* and *s-trans* monomer conformations in the transition state lead to the formation of *Z* and *E* anions, respectively. Further, in the presence of Li ion this pattern is repeated for the trimer anions **3** and is also plausible for the tetramer and higher anions. Thus, the lack of chain stereoregularity may correlate both with the intermediacy of both *E* and *Z* anions and a lack of specificity in monomer presentation.

Figure 1. Molecular weight distribution of poly(2-vinylpyridine) prepared by initiation with t-BuLi in toluene at −78 °C. $DP_n = 38$; $M_w/M_n = 2{\cdot}7$; [t-BuLi] = $2{\cdot}5 \times 10^{-3}$ M.

The above shows clearly that intramolecular cation coordination does not necessarily lead to stereoregular vinyl polymerization, let alone to highly isotactic polymers. However, it could be argued that polymerizations in THF are inherently less stereoregular, perhaps as a result of a lack of strong monomer coordination to Li ion in the transition state due to competitive Li solvation by THF. This prompted us to investigate the 2-VP polymerization stereochemistry in toluene at −78 °C. Thus, in toluene 2-VP coordination to Li should be stronger and the intramolecular chelation of Li^+ occurring at the chain end anion should be even more pronounced. Earlier investigations had shown the formation of isotactic polymers, especially in the presence of Mg counter ion.[30–32] Thus, polymerization of 2-VP initiated by Grignards or benzylpicolylmagnesium has been shown to lead to the formation of fairly highly isotactic polymers (*mm* = 0·92).

Preliminary studies carried out in toluene at −78 °C with n-BuLi or t-BuLi as initiators indeed showed the formation of predominantly isotactic P2VP (*mm* ≈ 0·70).[33] However, the use of carefully sublimed t-BuLi gave atactic polymers with syndiotactic content of about 44%. Initiator efficiencies were rather low (40–50%) so that unreacted t-BuLi is present. Trimodal distributions were obtained in most cases showing that at least three different species may have contributed to the polymerization process (Figure 1). Further, the polymer tended to precipitate during the polymerization, so this may have contributed to the width of the MW distribution. However, trimodal distributions were also observed at low conversions and before polymer precipitation occurred.

The lack of solubility of P2VP at −78 °C was addressed by initiation of 2VP by polystyryllithium initiated by t-BuLi in toluene. In this case, a soluble block copolymer was obtained bu the MWD was still trimodal and the stereochemistry of the P2VP block was unchanged. Viscometric measurements on toluene-soluble PS–P2VLi block copolymers showed an absence of polymer aggregation at 25 and −78 °C.[34]

Table 6. Molecular weight distribution and stereochemistry of P2VP synthesized with various lithium initiators in toluene at −78 °C[a]

Initiator	Heterogeneous	[t-BuOLi]/[BuLi]	MWD[d]	Initiator efficiency (%)[e]	*mm*	*mr*	*rr*
t-BuLi	Yes	—	4·0	60	0·20	0·36	0·44
t-BuLi	No	—	2·7	42	0·22	0·37	0·41
PS-Li[b]	No	—	3·5	40	0·23	0·35	0·42
PS-Li[c]	No	—	1·2	>90	0·22	0·38	0·40
t-BuLi–t-BuOLi	Yes	2·1	1·4	54	0·72	0·18	0·10
PS-Li–t-BuOLi[c]	No	2·1	1·2	>90	0·74	0·15	0·11
PS-Li–t-BuOLi[b]	No	2·1	1·4	40	0·74	0·16	0·10

[a] Initiator concentration around $2{\cdot}3 \times 10^{-3}$ M.
[b] Addition of styrene to t-BuLi at 0 °C.
[c] Addition of t-BuLi to 1,1-diphenylethylene (DPE) followed by styrene.
[d] SEC analysis using P2VP standards. Number-average molecular weights 5900–12,900.
[e] Calculated at M_n(calc)/M_n(exp).

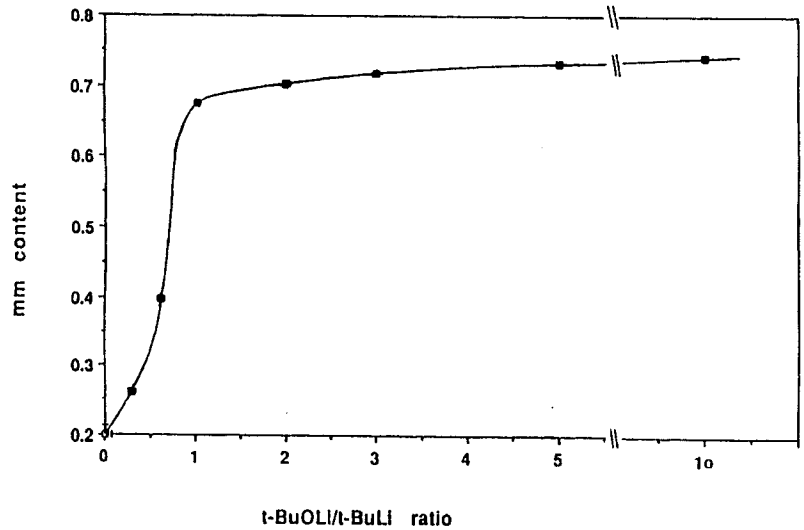


Figure 2. Fractional isotactic content of poly(2-vinylpyridine) as a function of the t-BuOLi/t-BuLi molar ratio in toluene at −78 °C

Thus, the propagating chains were not associated into dimers or higher aggregates although cross-association with t-BuLi was still possible. In order to evaluate this factor, t-BuLi in toluene was first reacted with 1,1-diphenylethylene and subsequently styrene before addition of 2VP. 1,1-Diphenylethylene is known to react quantitatively with t-BuLi.[35] After termination (CH_3OH) the P2VP was found to have a narrow molecular weight distribution (Table 6) and initiator efficiencies were close to quantitative.

This suggests that the multimodal distributions observed in the absence of 1,1-diphenylethylene were due to the presence of P2VPLi–t-BuLi aggregates.[36] Hence the trimodal distributions observed even at low conversions were apparently due to complexes of P2VPLi and t-BuLi. In fact, the relatively low initiator efficiencies were thus most likely due to the lower reactivity of the t-BuLi in the P2VPLi–t-BuLi complexes. This would account for the initiator efficiencies being generally around 50% (Table 6).

Interestingly, the stereochemistry of polymerizations initiated with purified t-BuLi was identical for all systems studied, indicating that the formation of P2VPLi–t-BuLi complexes did not change the stereochemistry of polymerization. This was also shown by fractionation of some of the polymers having trimodal distributions. No tacticity differences were observed between high- and low-MW fractions. Apparently the reactivity, but not the stereochemistry, of the P2VPLi was affected by complex formation with t-BuLi.

We next turned out attention to the formation of isotactic P2VP initiated with impure t-BuLi. Since in the presence of O_2 the formation of t-BuOLi is possible, we decided to investigate the effect(s) of addition of

Table 7. Effects of lithium alkoxides on the stereochemistry for the t-BuLi-initiated polymerization of 2-VP in toluene at −78 °C[a]

Expt No.	ROL i	[ROLi]/[t-BuLi]	Stereochemistry[b]			
			mm	*mr*	*rr*	ρ[c]
1	—	—	0·36	0·44	1·3	
2	t-BuOLi	0·6	0·40	0·31	0·29	1·5
3	t-BuOLi	1·0	0·69	0·20	0·11	1·7
4	t-BuOLi	2·0	0·71	0·17	0·12	1·7
5	t-BuOLi	5·0	0·73	0·17	0·10	1·8
6	t-BuOLi	10·0	0·76	0·14	0·10	1·9
7	t-BuOLi	2·0[d]	0·74	0·17	0·09	1·8
8	t-BuOLi	2·0[e]	0·69	0·20	0·14	1·7
9	t-BuOLi	2·0[f]	0·62	0·23	0·15	1·6
10	MeOLi	2·6	0·27	0·36	0·37	1·4
11	EtOLi	1·5	0·28	0·35	0·37	1·4
12	i-C_3H_7OLi	2·1	0·40	0·28	0·32	1·7
13	EtOLi–t-BuOLi	1·1/2·2[g]	0·46	0·30	0·24	1·6
14	1-AdamOLi[h]	4·1	0·87	0·07	0·06	2·5

[a] [t-BuLi] = $2{\cdot}0\times10^{-2}$–$2{\cdot}3\times10^{-2}$ M.
[b] Calculated by pentad analysis of C-2 carbon NMR.
[c] Persistence ratio defined as $\rho = 2(m)(r)/(mr)$ where $(m) = (mm) + (mr)/2$.
[d] [t-BuLi] = 5×10^{-3} M.
[e] [t-BuLi] = 5×10^{-4} M.
[f] [t-BuLi] = 5×10^{-5} M.
[g] EtOLi added after t-BuOLi.
[h] Lithium salt of 1-adamantol.

t-BuOLi on the t-BuLi initiated polymerization of 2VP.[38] Figure 2 shows the pronounced effect on the *mm* content of t-BuOLi (Figure 2). There is a steep increase in isotactic content. The sharp break at a ratio of one indicated the formation of a 1:1 P2VPLi–t-BuOLi complex. It is also of interest to note that Li salts of simple primary and secondary alcohols are virtually completely ineffective in enhancing isotactic content (Table 7). In order to establish whether this failure to affect stereochemistry was due to a lack of complex formation, the following experiment was carried out. A t-BuLi–t-BuOLi initiator system was prepared in the molar ratio of 1:2·3. The polymerization in this case yielded a P2VP with a tacticity of about 70% (Table 7). The presence of an additional 1·1 equivalent (with respect to t-BuLi) of EtOLi during this polymerization dramatically lowers the isotactic content of the P2VP formed (Table 7, run 13). This and similar experiments indicated that the formation of P2VPLi–EtOLi complexes is competitive with the formation of P2VPLi–t-BuOLi complexes. This is not unexpected since the formation constant of P2VPLi–lithium alkoxide complexes is expected to decrease with increasing alkyl size.

Therefore, an attempt was made to evaluate the role of concentration on stereochemistry for the t-BuLi–t-BuOLi–2-VP system.

According to equation (6), the fraction of complex would be expected to decrease as the total concentration of anion decreases at constant t-BuOLi/t-BuLi ratio. The results of such experiments, shown in Table 7 (runs 7–9), clearly show that the *mm* content decreases with decreasing anion concentration, consistent with equation (6).

$$\text{P2VPLi} + \text{t-BuOLi} \rightleftharpoons \text{P2VPLi}\cdot\text{t-BuOLi} \qquad (6)$$

In order to check the validity of equation (6) further, viscosity measurements of P2VPLi were carried out in the absence and presence of t-BuOLi at −78 and 25 °C in toluene. Just as for the systems without t-BuOLi, the experiments were carried out with PS–P2VPLi block copolymers. In all cases, the viscosities before and after termination with CH_3OH were found to be equal, so that clearly there is only cross-association with t-BuOLi according to equation (6).

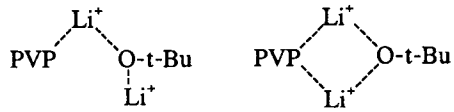
These results indicate that in this case polymer anion aggregation is not a factor in controlling stereochemistry. Molecular weight distributions in toluene at −78 °C in the presence of t-BuOLi were narrow (Table 6), indicating the participation of a single species or of several species interconverting rapidly on the reaction time-scale. Since t-BuOLi in toluene is tetrameric,[36,39] the formation of aggregated species according to

$$\text{PVPLi} + (\text{t-BuOLi})_4 \rightleftharpoons \text{PVPLi}\cdot(\text{t-BuOLi})_n + (1 - 0{\cdot}25n)(\text{t-BuOLi}) \qquad (7)$$

$$n = 1\text{–}3$$

cannot be ruled out. In fact, such species have been demonstrated by Wang *et al.*[39] in mixtures of lithio isobutyrates and t-BuOLi in toluene. However, the relatively sharp break in the plot of isotactic content against [t-BuOLi]/[t-BuLi] ratio indicates that the stereochemistry of multiple aggregates, if present, is not very different.

The formation of PVPLi·t-BuOLi complexes is not surprising given the affinity of the Li ion for neutral oxygen donors such as THF. Certainly charged oxygen anions would be even better coordinating agents. The simplest PVPLi·t-BuOLi complex could form structures such as **18** and **19**.



18 **19**

Structures such as **19** have been proposed in t-BuOLi complexes of lithio isobutyrates.[37-41] Based on the reduced initiation and polymerization rates in the presence of t-BuOLi in toluene,[42] we favor species **19** since the presence of an additional electrophilic lithium at the carbanion center is expected to reduce anion reactivity while the reactivity of structure **18** would not be expected to be lowered. Structure **18** is also more consistent with the remarkable effects of alkyl structure of ROLi on the polymerization stereochemistry.

The stereochemical effects of the addition of t-BuOLi is of considerable interest, in particular the pronounced effects of the degree of substitution of the secondary hydrogen of $(CH_3)_2CHOLi$ by methyl, raising the *meso* content of the chain from 54 to 82%. Addition of other lithium alkoxides such as lithium adamantoxide gives rise to even higher isotactic content (*mm* = 0·87) (Table 7, run 14).

It should be pointed out that in all of these cases, the isotactic content of P2VP was evaluated using a set of modified C-2 assignments that tend to give a lower isotactic content. By using the previous assignments, isotactic contents would be even higher (for instance, 93% rather than 87%).[26]

DISCUSSION

It is of interest to note that addition of lithium alkoxides in the anionic polymerizations of MMA[43,44] and even of styrene[45] have led to enhanced isotactic content.[39-43] The latter case is interesting in that addition of t-BuOLi in hexane at −30 °C gave rise to a relatively small fraction of highly isotactic polystyrene. This suggests that, at least in principle, isotactic control is possible in the absence of coordination of Li ion to penultimate Lewis bases. This would suggest a model introduced above in which the fraction of meso dyads is determined both by the relative stabilities of pro-*meso* and pro-racemic ion pairs, by the selectivity of electrophilic attack (*syn* or *anti*) and by the corresponding rate constants of monomer addition (Scheme 2).

In the presence of t-BuOLi–P2VPLi complexes, it is possible that the equilibrium between the two pro-chiral species is shifted toward the pro-*meso* form perhaps as a result of non-bonding interactions in the pro-racemic complex (Scheme 2). Assuming syn attack only, as seems reasonable, and provided that interconversion between the two pro-chiral ion pairs is rapid compared with monomer addition, as seems likely, the fraction of *meso* dyads is given by

$$m = \frac{\mathrm{d}(m)\,\mathrm{d}t}{\mathrm{d}(m)/\mathrm{d}t + \mathrm{d}(r)/\mathrm{d}t} = \frac{k_\mathrm{m}}{k_\mathrm{m} + Kk_\mathrm{r}} \qquad (8)$$

Since the probability of *meso* dyad formation according to equation (8) is a constant, this would lead to Bernoullian statistics. This is not in agreement with the data in Table 6 that show persistence ratios well in excess of one. Thus, long sequences of *m* dyads are present. Since there is no evidence for the participation of two separate propagating species, a Coleman–Fox mechanism is unlikely.[46] This then raises the possibility of a Markoff-like process in which the stereochemistry of the dyad adjoining the anion affects the stereochemistry of addition. A particular kind of such a process would be one in which isotactic growth occurs in a helix, a typical conformation for isotactic polymers. Inspection of CPK models of such propagating helices indicate that the complexed t-BuOLi may be more readily complexed to the pro-*meso* face of the anion compared with the complex at the pro-racemic face. We are currently exploring predictions of such a model regarding the effects of substitution of the t-Bu group with other suitable sized groups.

CONCLUSIONS

The intramolecular coordination of Li, MgX and other counter ions with penultimate Lewis bases (esters, pyridines, etc.) in anionic vinyl polymerizations in hydrocarbon media has long been advocated to account for the formation of isotactic PMMA and P2VP.

The present research demonstrates such interactions for models of anionic P2VPLi in THF including unambiguously the ΔH and ΔS of intramolecular chelation and this accounts well for the high stereoselectivity of a variety of simple alkylation and other electrophilic reactions. However, in THF the anionic polymerization of 2-VP initiated by lithium carbanions leads only to slightly isotactic polymers and in carefully purified systems the polymerization in toluene gives slightly syndiotactic P2VP! These results show that our current models are inadequate to account for isotactic control in the anionic polymerizations in non-polar media of MMA, 2-VP and similar monomers.

In the presence of 1–4 equivalents of t-BuOLi and

other tertiary lithium alkoxides, isotactic polymerization of 2VP is possible ($mm \leq \sim 90\%$) and is due to the formation of 1:1 P2VPLi·ROLi complexes. The narrow molecular weight distributions obtained and the viscometric studies of the PVPLi show that P2VPLi and its 1:1 complexes are monomeric in toluene. Analysis of the stereochemistry of the isotactic P2VP shows the presence of long isotactic sequences. The stereochemistry apparently depends on subtle steric interactions between the pro-chiral anion and the alkyl groups of the $(ROLi_2)^+$ 'counter ion' which shifts the equilibrium between the diastereoisomeric pro-*meso* and pro-racemic ion pairs in favor of the pro-*meso* species which reacts with the monomer in *syn* fashion to produce *meso* sequences. A helical chain conformation at the chain end is expected to favor such a pro-*meso* species, further leading to rapid isotactic chain growth.

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