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Effects of Lithium Bromide on the Glass Transition Temperatures of Linear and Macrocyclic Poly(2-vinylpyridine) and Polystyrene

Yaodong Gan, Dahai Dong, and
Thieo E. Hogen-Esch*

Loker Hydrocarbon Institute, Department of Chemistry,
University of Southern California,
Los Angeles, California 90089-1661

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Introduction

We have reported previously that the values of the glass transition temperature (T_g) of macrocyclic poly(2-vinylpyridine) (P2VP) increase with decreasing molecular weight (MW), consistent with entropy calculations.[1−4] This increase in T_g was interpreted as reflecting the increased conformational stiffness of the macrocycles as the degree of polymerization (DP) decreased.[1−3] Differences in T_g were reported as large as 40 K between linear and macrocyclic P2VP around a DP of 40.[2] These differences in T_g were observed to disappear at a DP of around 200.

However, the poly(2-vinylpyridine) macrocycles were synthesized by reacting the lithium dianion "living" precursors with 1,4-bis(bromomethyl)benzene (1,4-DBX), thus generating LiBr, and the polymers were isolated by precipitation in hexane. Therefore, it is possible that the LiBr present in the polymer matrix may have increased the glass transition temperature of the P2VP macrocycle, for instance, by coordination of one or more pyridine groups to the Li cation. Such coordination processes are well documented for poly(ethylene oxide) (PEO) and were demonstrated to affect the DSC behavior and conductivity of the PEO matrix.[5−7] Effects of added $LiClO_4$ on the T_g of PEO−P2VP blends were recently observed.[8,9]

Therefore a study of the possible effects of LiBr on the T_g of linear and macrocyclic P2VP seemed of interest. In order to evaluate the occurrence of salt effects unrelated to the direct coordination of the P2VP pyridine nitrogens with Li ion, we also investigated the effect(s) of LiBr on the T_g of linear polystyrene (PS) since this polymer resembles P2VP with regard to both structure and thermal properties but does not specifically coordinate the Li cation.

Experimental Section

Synthesis. The anionic polymerization of 2VP, the end to end cyclization, and the fractionation of cyclic P2VP have been described previously.[1−3] A series of monodisperse linear P2VP's and fractionated cyclic P2VP's with the same molecular weight were prepared. The cyclic P2VP samples prepared by this method contained a certain amount of LiBr, which was removed by precipitation in water followed by centrifugation and drying. The resulting polymer was redissolved in THF and then precipitated in hexane. Macrocyclic PS was synthesized by initiation of styrene in THF at about −70 °C using lithium naphthalene as initiator. Styrene was distilled into the reactor under high vacuum over about 1 h. After completion of the polymerization, an aliquot of the PS dianion precursor was withdrawn and protonated (by CH_3OH) to serve as an isobaric linear PS sample. Cyclization of the remaining PS dianion with 1,4-bis(bromomethyl)benzene (DBX) was performed under high vacuum at −70 °C and at low carbanion concentration (<3×10^{-4} M). DBX (TCI America, Inc.) was recrystallized in $CHCl_3$ several times (mp 145−146 °C). Both linear and macrocyclic PS samples were obtained by precipitation in excess methanol.

Table 1. Apparent Molecular Weights (MW) and Glass Transition Temperatures (T_g) of the Unpurified and Purified Cyclic (C) and Linear (L) P2VP of Identical Degrees of Polymerization

$M_p(L)$[a]	$D(L)$[b]	$T_g(L)$ (°C)	$M_p(C)$[c]	$D(C)$	$T_g(C)$ (°C) unpurified	$T_g(C)$ (°C) purified	$\langle G\rangle$[d]
1900	1.12	58.0	1590	1.05		95.9	0.84
4220	1.08	85.3	3410	1.04	116.6	99.1	0.81
6610	1.21	89.9	4800	1.10	105.0	98.7	0.73
18970	1.16	97.3	14570	1.15	98.2	99.7	0.77

[a] SEC peak molecular weight (MW) for a linear precursor (L). [b] $D = M_w/M_n$. [c] Apparent MW for fractionated cyclic polymer (C) determined by SEC. [d] Ratio of $M_p(C)$ to $M_p(L)$.

Sample Preparation. Anhydrous LiBr (Aldrich; 15.00 mg) was dissolved in 10.0 mL of methyl alcohol (MeOH). Aliquots of 0.0, 0.2, 0.4, 0.8, 1.6, 2.4, and 4.0 mL of the LiBr/MeOH solution were transferred to seven sample vials each containing 40.0 mg of P2VP, and methanol was added to each vial to give 4.0 mL of solution. After the solvent was removed, the samples were dried in vacuo for 2 days at 50−60 °C. In the case of PS, due to its poor solubility in MeOH, THF was used as the solvent in order to obtain the LiBr-containing PS samples.

Measurements. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer System-4 Thermal Analyzer under a nitrogen atmosphere. The instrument was calibrated with indium (mp = 156.60 °C) before and after use. All samples (20−30 mg) were sealed in aluminum pans and preheated from 40−50 to 140−150 °C at a rate of 20 °C/min and cooled to 40−50 °C at a rate of −20 °C/min in order to assure identical thermal treatments, and then they were heated to 140−150 °C at a rate of 20 °C/min. The DSC analyses were carried out two to three times. Reproducibility was found to be within 1 °C. The glass transition zone was determined as the temperature range between two intersection points of the base lines with the extrapolated sloping portion of the DSC curves, the value of T_g being defined as the midpoint of the heat capacity change.

SEC Analysis. Size-exclusion chromatography (SEC) was carried out by using THF as the eluting solvent at 1.0 mL/min. One percent by volume of triethylamine was added to THF in order to prevent adsorption of P2VP onto the column. Molecular weight calibration was done using narrow molecular weight distribution P2VP and PS standards (Polysciences, Inc.).

Results and Discussion

In order to evaluate the effect(s) of LiBr on the T_g of macrocyclic P2VP, the four P2VP macrocycles having DP's of 19−190 were first synthesized and then fractionated. The fractionation procedures involved repeated addition of hexane to THF solutions of the macrocyclic P2VP followed by filtration to remove high MW "polycondensation" products.[1,2] The THF solutions of the resulting narrow MW distribution P2VP macrocycles (Table 1) were then divided into two sets. One set was precipitated in hexane and then analyzed by DSC. The other identical set of samples was precipitated in water to remove LiBr followed by centrifugation and drying. In order to eliminate any solvent effects on T_g, the samples were then redissolved in a small amount of THF reprecipitated in hexane and analyzed by DSC. The isobaric linear P2VP samples obtained by protonation of the P2VP precursor dianion were also precipitated in hexane (Scheme 1).

Multiple reprecipitation in water did not affect the T_g value of the P2VP macrocycles. A P2VP macrocycle of a DP of 42 was used to carry out studies on the effects

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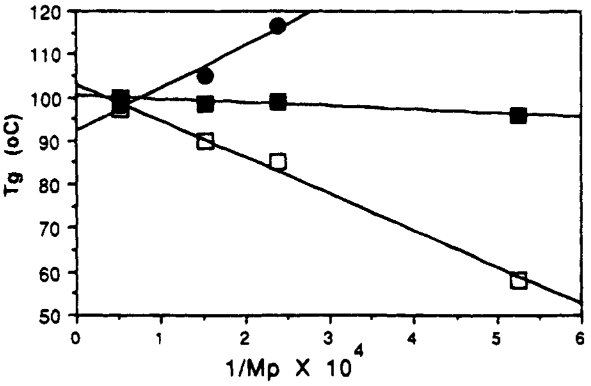
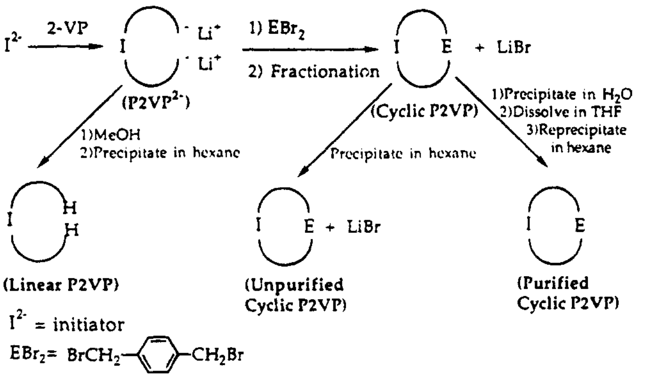


Figure 1. T_g of linear (□), unpurified cyclic (●), and purified cyclic (■) P2VP as a function of $1/M_p$: (□, ●) precipitated in hexanes only; (■) precipitated in H_2O followed by dissolution in THF and reprecipitation in hexanes.

Scheme 1. Synthesis of Linear and Macrocyclic P2VP's and Purification of Cyclic P2VP



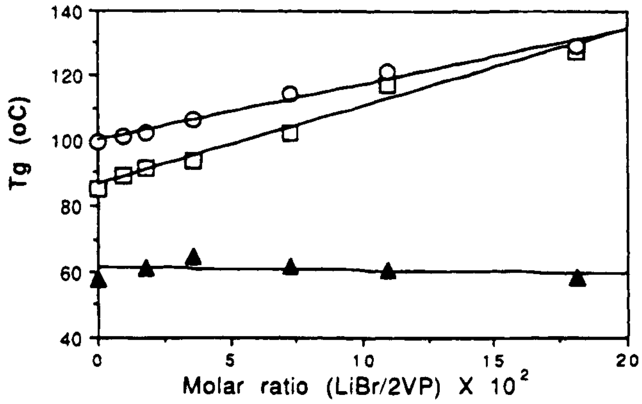


Figure 2. Effects of LiBr on the T_g of matched linear (□) and macrocyclic (○) P2VP of M_p = 4200 and linear PS (▲) of M_p = 4000.

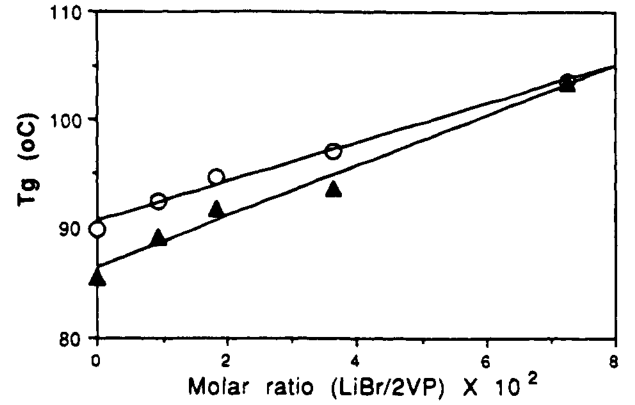


Figure 3. Effects of LiBr on the T_g of linear P2VP: (▲) M_p = 4200; (○) M_p = 6600.

of added LiBr on T_g. Some of this sample containing LiBr was later reprecipitated in water. DSC analysis of this polymer sample showed that the T_g value was identical with that of the macrocycle before addition of LiBr.

Plots of T_g against $1/M_p$ of the linear and isobaric unpurified, and purified P2VP macrocycles are shown in Table 1 and Figure 1. The unpurified cycles show increasing T_g values with decreasing DP as observed previously. The purified P2VP macrocycles show essentially no variation of T_g with DP, with a slight decrease of about 5 °C for the macrocycle having a DP of about 20.

It is clear that the differences in T_g between the purified and unpurified P2VP macrocycles are related in part to the absence and presence of LiBr.

However, T_g differences between purified macrocyclic and linear P2VP, although smaller than reported before, remain appreciable, increasing with decreasing DP to a value of about 38 °C at a DP of 20. In order to document these effects further, LiBr blends of linear and macrocyclic P2VP of a DP of 42 were prepared and analyzed by DSC (Figure 2). In both cases a linear relationship is obtained between T_g and LiBr content. The slope for the macrocycle is clearly lower than that of the linear P2VP. In order to confirm that the observed variation in T_g is related to the presence of the 2-pyridyl groups, similar LiBr blends were prepared for a linear polystyrene of approximately the same DP (=40) (see the Experimental Section). In this case LiBr has no effect on T_g.

The above data confirm that the apparent increases in T_g with DP of the unpurified P2VP macrocycles are related to the presence of LiBr. Coordination of Li cation to one or multiple pyridine nitrogens is expected to substantially reduce the mobility of the chain, and this reduction is expected to be larger for the linear than for the macrocyclic P2VP since the linear chain is conformationally less restrained and hence undergoes a greater loss of mobility upon coordination.

The effect of the addition of LiBr on the T_g values of linear P2VP's of different DP's is shown in Figure 3. The slope again is greater for the lower MW sample (DP = 42) probably for the same reason as the corresponding effects for the matched linear–macrocyclic pair of Figure 2. The T_g of the longer less mobile chains is clearly less affected by the presence of LiBr.

It is of interest to note that, in the DSC plots of the P2VP–LiBr systems (Figure 4), the width of the thermal transitions increases with increasing LiBr concentration. Thus the P2VP macrocycle (DP = 42) in the presence of a low concentration of LiBr shows a relatively narrow T_g transition (about 8 °C). In the presence of 0.182 mol equiv of LiBr, however, the width of the transition is increased to about 43 °C. Similar results were found for linear P2VP but not for linear polystyrene. This may indicate the presence of P2VP chain segments having a wide spectrum of mobilities consistent with a variety of microenvironments resulting from different degrees of coordination of the pyridine groups. Effects of even higher LiBr contents unfortunately could not be studied since the glass transition region began to overlap with a large endotherm at around 180 °C.

In principle, the above results could be used to estimate the salt content of the unpurified macrocycles. For instance, for the unpurified macrocycle (DP = 42) a salt content of 10 mol % (with respect to 2VP units)

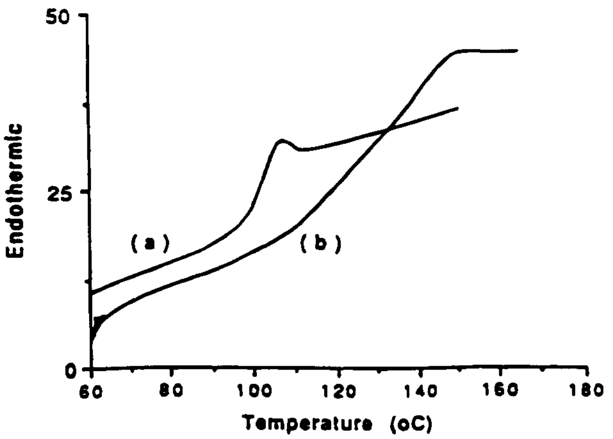


Figure 4. DSC thermograph of cyclic P2VP (DP = 42) containing (a) 0.75 wt % LiBr and (b) 15 wt % LiBr.

Table 2. Apparent Molecular Weight (MW) and Glass Transition Temperatures (T_g) of Linear Polystyrene (PS) and Cyclic PS with Identical Degrees of Polymerization

$M_p(L)^a$	$D(L)^b$	$D(C)^c$	$T_g(L)$ (°C)^d	$T_g(C)$ (°C)^d	$\langle G\rangle^e$
1660	1.35	1.37	63	70	0.82
2500	1.11	1.12	68	88	0.79
4100	1.14	1.18	80	100	0.74
8500	1.06	1.11	89	100	0.73
22000	1.04	1.08	98	100	0.78
43000	1.24	1.28	100	100	0.79
73000	1.03	1.07	100	100	0.81

[a] SEC peak molecular weight (MW) for a linear precursor. [b] $D(L) = M_w/M_n$ of a linear precursor. [c] $D(C) = M_w/M_n$ of a fractionated cyclic polymer. [d] Reproducibility ±1.0 °C. [e] Ratio of $M_p(C)$ to $M_p(L)$.

was determined from the apparent T_g value. This is considerably higher than calculated on the basis of the reaction stoichiometry (~0.05 molar ratio LiBr/2VP). However, it should be pointed out that the macrocycles are recovered by repeated precipitation of the high-MW side products resulting from intermolecular reactions. During this fractionation process, hexane is added dropwise to a THF solution of the crude cyclization product and higher MW P2VP is then first precipitated out. At this point, the resulting solution containing a large fraction of THF will dissolve most of the LiBr salt. It is likely therefore that the LiBr was inadvertently concentrated in the low MW macrocycles.

For the same amounts of monomer and solvent, the formation of high-MW cyclic P2VP (DP = 190) requires less initiator and coupling agent, so that less LiBr is produced. As a result the T_g values of purified and unpurified P2VP (DP = 190) are found to be essentially identical.

Because of the structural similarity of P2VP and PS, the determination of the T_g behavior of PS macrocycles as a function of DP was of obvious interest.[10] Consequently, we prepared a number of PS macrocycles that were synthesized using techniques similar to that used for macrocyclic P2VP (Table 2).[11] In this case the presence of LiBr in the PS macrocycles is not anticipated since LiBr is highly soluble in methanol, the precipitating solvent for polystyrene (see the Experimental Section).

The corresponding T_g vs MW plots for macrocyclic and linear PS show patterns that are very similar to that observed for the case of purified macrocyclic and linear P2VP (Figure 5). Starting at high DP there is essentially no change in the T_g of macrocyclic PS as the DP decreases until a DP of about 40, after which there is a rapid decrease to a T_g of 86 °C at a DP of 20.

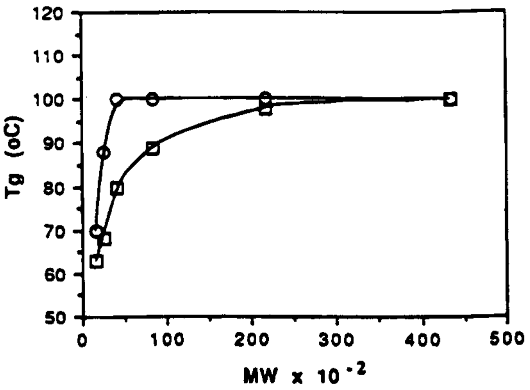


Figure 5. T_g's of linear (□) and cyclic (○) polystyrene as a function of MW.

For both the P2VP and PS cases the difference in glass transition temperature, ΔT_g, between linear and macrocyclic polymers increases with decreasing DP as concluded previously.[2] It is not clear to what degree this increase in ΔT_g is due to the absence of end groups in the macrocycles and to the increasing stiffness of the macrocycles as the DP decreases.

The availability of even lower DP macrocycles would be helpful in this regard. Unfortunately the differentiation between linear and macrocyclic polymers, for instance, by SEC, is difficult since the difference in hydrodynamic volumes appears to narrow appreciably below a DP of about 20 as indicated by SEC (Table 1). Thus other characterization methods will have to be found. This is currently under study.

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