January, 1987] © *1987 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., **60**, 405—407 (1987)* 405

# Viscosity Behavior of Poly(2-vinylpyridine) of a Low Molecular Weight

Masafumi Yoshida,* Kikuo Itoh, Noriyuki Sakamoto, and Shizuo Arichi
Department of Chemistry, Faculty of General Education, Kumamoto University,
Kurokami 40-1, Kumamoto 860

(Received May 28, 1986)

**Synopsis.** For the data of the limiting viscosity number of poly(2-vinylpyridine) of a low molecular weight $M_w$=2.26—0.21×10$^4$ in benzene and methanol, the value of the thickness parameter, $b$, and the energy difference, $E$, between the gauche and trans state were discussed in terms of the theory of Rossi and Perico. It is possible to use this theory for the viscosity data in the molecular weight range of 0.35—1.30×10$^4$. The values of $E$ and $b$ were thus estimated; $E$ depended on the nature of the solvent for this polymer, while $b$ was constant (0.3 nm). The temperature dependence of the calculated limiting viscosity number, $\mathrm{d}\ln[\eta]/\mathrm{d}T$, in benzene and dioxane was discussed, together with the measured values.

In the relation of the limiting viscosity number and the molecular weight for the range of low molecular weights, the equation $[\eta]=KM^{0.5}$ holds. Here, the constant, $K$, is independent of the nature of a solvent.[1] For poly(2-vinylpyridine), the present authors previously reported that the constant, $K$, is equal to the value of Flory's $K_\theta$, which is itself related to the unperturbed mean-square radius gyration of the chain molecule.[2] Consequently, it was deduced that it was possible to evaluate the characteristic ratio from the measurement of the limiting viscosity number for a low molecular weight.

On the other hand, according to the precepts of statistical mechanics, the properties of chain molecules should be evaluated by averaging all the conformations generated by varying all angles and all bond lengths to the extent permitted by the chain structure. The subsequent calculation for a long chain, is indeed formidable, but they can be greatly abbreviated though the adoption of a rotation angle.[3] Furthermore, Rossi and Perico reported the theoretical treatment of a short-chain polymer.[4] They showed that the limiting viscosity number of a short-chain polymer could be evaluated from a model of the independent hindered rotation by introducing $b$, a thickness parameter.

In this paper, the energy difference, $E$, between the gauche and trans states and thickness parameter, $b$, will be discussed on the basis of the limiting viscosity number for the low-molecular-weight range of poly(2-vinylpyridine) in benzene and methanol, using the theory of Rossi and Perico.[4] These values in several solvents will then be evaluated, and the temperature dependence of the calculated limiting viscosity number will be discussed.

## Experimental

Poly(2-vinylpyridine) was polymerized, with butyllithium as the initiator, in tetrahydrofuran at −27 °C for the BL-sample, while A-1-V was polymerized with αα′-azobisisobutyronitrile in benzene at 25 °C. The polymer samples were obtained by the method of fractional precipitation. Benzene and petroleum ether were used as solvent and precipitant. The limiting viscosity number was measured with a Ubbelohode-type viscometer.

The weight average molecular weight of the polymer fraction was determined with a Fica-50 automatic light scattering photometer in methanol at 25 °C for scattered angles of 30—150°. The measurement of the specific refractive-index increment was carried out by the use of a Shimadzu-DR-3-type differential refractometer.

## Results and Discussion

The relation of the limiting viscosity number and the molecular weight for short chain polymers was represented by the theory of Rossi and Perico.[4] The relation was as follows:

$$[\eta] = \phi 6^{3/2}(R_s^3/M)$$
$$R_s = \langle s^2\rangle_0^{1/2} + b$$

Table 1. Results from the Calculation and the Viscosity Measurements

| Sample | $M_w\times10^{-3}$ | $N_c$[a] | $\langle s^2\rangle_{0,\,\mathrm{calcd}}^{1/2}$[b] nm | Benzene | | $\langle s^2\rangle_{0,\,\mathrm{calcd}}^{1/2}$[c] nm | Methanol | |
|---|---|---|---|---|---|---|---|---|
| | | | | $[\eta]_{\mathrm{calcd}}$ | $[\eta]_{\mathrm{meas}}$ | | $[\eta]_{\mathrm{calcd}}$ | $[\eta]_{\mathrm{meas}}$ |
| BL-6-2 | 22.9 | 435 | 3.61 | 0.110 | 0.111 | 4.04 | 0.151 | 0.170 |
| BL-6-3 | 13.1 | 249 | 2.70 | 0.0869 | 0.089 | 3.01 | 0.117 | 0.117 |
| BL-6-4 | 9.46 | 179 | 1.98 | 0.0748 | 0.075 | 2.51 | 0.0989 | 0.099 |
| BL-6-5 | 7.49 | 141 | 1.98 | 0.0671 | 0.065 | 2.19 | 0.0874 | 0.086 |
| BL-6-6 | 5.46 | 103 | 1.66 | 0.0582 | 0.057 | 1.83 | 0.0747 | 0.074 |
| BL-6-7 | 4.95 | 93 | 1.57 | 0.0557 | 0.055 | 1.72 | 0.0702 | 0.073 |
| BL-6-8 | 3.55 | 67 | 1.29 | 0.0478 | 0.043 | 1.41 | 0.0594 | 0.057 |
| BL-6-9 | 2.10 | 39 | 0.92 | 0.0336 | 0.039 | 0.99 | 0.0397 | 0.043 |

a) Bond number of the polymer chain. b) and c) A root mean-square radius gyration for $E$=1.0 and 1.15 kcal mol$^{-1}$ respectively. (1 cal=4.184 J).

where $\phi$ was a hydrodynamic parameter and was constant ($2.87\times10^{21}$) for the number of monomeric units $N_c>20$; M was the molecular weight. $<s^2>_0$ was a mean-square radius gyration and was calculated for the chain with an independent bond rotational potential according to the rotational-isomer method[5]; $b$ was the thickness of the polymer chain.

The limiting viscosity number for a low molecular weight was calculated by choosing the appropriate values of $E$ and $b$ yielding the best-fitting point. In Table 1 the calculated results are shown, together with the measured values, which have been reported before in benzene and methanol at 25 °C.[2] The calculated values were in very good agreement with all the measured values except with the data of BL-6-2 in methanol and with those of BL-6-9 in both solvents. The value of $E$ is 1.0 kcal mol$^{-1}$ in benzene and 1.15 kcal mol$^{-1}$ in methanol. As to the disagreement with the value of $E$ in benzene and methanol, it is possible to explain it as follows. The specific interaction between poly(2-vinylpyridine) and a solvent was investigated; alcohol is solvated to the pyridine nitrogen of this polymer through hydrogen bonding. However, there has been no report of the specific interaction in benzene for this polymer. On the other hand, the value of $b$ is the same, 0.3 nm, in both solvents (the size of the pyridine ring: 0.3 nm). This value is reasonable. Furthermore, the relation of the calculated limiting viscosity number and the molecular weight is represented by the Mark-Houwink-Sakurada empirical equation: $[\eta]_\theta=K_\theta M^{0.5}$ That is, $E$ is affected by the nature of a solvent, but $b$ is independent of this polymer.

As to the discrepancy between the calculated and measured viscosity data of BL-6-2 in methanol and BL-6-9 in both solvents, it may be explained that, for the former, the theory of Rossi and Perico can not be accepted because of the presence of the excluded volume;[2] as for the latter, it is difficult to determine the accurate limiting viscosity number for very a low viscosity.

From the above conclusion that $b$ is independent of the nature of a solvent, it is possible to evaluate $E$ from one point of the limiting viscosity number over the suitable-molecular weight range: 3500—13000 for this polymer. Consequently, the value of $E$ is calculated from the data of BL-6-7 in ethyl methyl ketone and dioxane and from those of A-1-V ($M_w=7.87\times10^3$) in ethanol and chloroform.[7] The value of $E$ in ethyl methyl ketone and dioxane, which are very poor solvent for this polymer, are 0.95 and 1.05 kcal mol$^{-1}$ respectively. On the other hand, in ethanol, $E$ is 1.15 kcal mol$^{-1}$ and in chloroform, 1.25 kcal mol$^{-1}$.

**The Temperature Dependence of the Limiting Viscosity Number.** The temperature coefficient of the limiting viscosity number for poly(2-vinylpyridine) was previously reported from the temperature dependence on the limiting viscosity number.[2] Therefore, the limiting viscosity number could be calculated from the above equation at several temperatures. Table 2 shows the results of the calculated limiting viscosity numbers together with the measured limiting viscosity numbers (BL-6-7) in benzene, dioxane and ethyl methyl ketone at several temperatures. It is found that the calculated values agreed with the respective measured values. The values of the temperature coefficient of the limiting viscosity numbers, as calculated by means of the method of least squares, are $-5.1\times10^{-3}$ in dioxane, $-4.9\times10^{-3}$ in benzene, and $-4.6\times10^{-3}$ in ethyl metyl ketone. On the other hand, the measured values are $-4.5\times10^{-3}$ in dioxane, $-3.9\times10^{-3}$ in benzene, and $-3.7\times10^{-3}$ in ethyl methyl ketone. From the agreement with the calculated and measured limiting viscosity number and/or these temperature coefficients, it is considered that the theory of Rossi and Perico is acceptable and that the $E$ and $b$ values for the low-molecular-weight poly(2-vinylpyridine) are reasonable.

Flory's $K_\theta$ value of the polymer was indirectly determined in a non-$\theta$-solvent using an extrapolation method based on the two-parameter theory for a dilute solution. Flory's $K_\theta$ or $K$ value of a low molecular weight for a non-polar polymer is independent of the nature of a solvent at the same temperature; $E$ and $b$ are constant. The solvent effect on Flory's $K_\theta$ value of a polar polymer has also been investigated.[7]

The results of the investigation of poly(4-vinylpyridine) by Hirai and Yanagida indicate that the hydrogen bonding and solvation for the side chain of a polymer must result in an increase in the values of $E$ and $b$.[8] The values of $E$ and $b$ are 1.1—1.3 kcal mol$^{-1}$ and 0.45—0.67 nm respectively for poly(4-vinylpyridine). The values of $E$ and $b$ for that polymer are a little larger than those for the present observation, and $b$ is variable.

Table 2. Results from the Calculation and the Viscosity Measurements at Several Temperature

| Temperature | Dioxane | | Benzene | | Ethyl methyl ketone | |
|---|---|---|---|---|---|---|
| °C | $[\eta]^{a)}_{calcd}$ | $[\eta]_{meas}$ | $[\eta]^{b)}_{calcd}$ | $[\eta]_{meas}$ | $[\eta]^{c)}_{calcd}$ | $[\eta]_{meas}$ |
| 20 | 0.0618 | 0.0627 | 0.0570 | 0.0575 | 0.0526 | 0.0532 |
| 25 | 0.0601 | 0.0611 | 0.0555 | 0.0568 | 0.0512 | 0.0529 |
| 30 | 0.0584 | 0.0588 | 0.0540 | 0.0560 | 0.0500 | 0.0518 |
| 35.1 | 0.0569 | 0.0580 | 0.0526 | 0.0556 | 0.0487 | 0.0507 |
| 45 | 0.0541 | 0.0564 | 0.0502 | 0.0538 | 0.0466 | 0.0498 |
| 60 | 0.0504 | 0.0520 | 0.0469 | 0.0489 | 0.0437 | 0.0459 |

a) $E=1.05$ kcal mol$^{-1}$. b) $E=1.0$ kcal mol$^{-1}$. c) $E=0.95$ kcal mol$^{-1}$.

Now, the steric factor, $\sigma$, which is defined as the ratio between the actual steric hindrance, assuming a free rotation, is obtained from Flory's $K_\theta$ value. The effect of the substituent volume of the polymer chain on the value of is quite small-for example, polypropylene; 1.76, and polyisobutylene 1.80.[9] That is, the effect of the increase in the substituent volume, which results in the hydrobonding or solvation of this polymer, may not have an effect on $\sigma$ or on Flory's $K_\theta$ value. This is perhaps to be explained by the fact that, in a polymer chain, a huge group of atoms corresponding to the remaining part of the chain is always attached to the carbon atom being considered; therefore, the substituent volume may have only a minor effect on the hindering potential for rotation about the C–C bond. In other words, it is suitable that $b$ is constant and that the nature of the solvent affects the rotation of the chain.

In conclusion, the results of the above calculation suggest that the value of $E$ and $b$ can be evaluated from the limiting viscosity number of the low molecular weight for poly(2-vinylpyridine) in the range of 3500—13000 according to the theory of Rossi and Perico,[4] and that $E$ is affected by the nature of a solvent, while $b$ is constant.

## References

1) U. Bianchi and A. Paterson, *J. Polymer Sci., Part A-2*, **6**, 1759 (1968).

2) M. Yoshida, S. Yamaguchi, N. Sakamoto, and S. Arichi, *Bull. Chem. Soc. Jpn.*, **58**, 1023 (1985).

3) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York (1969).

4) C. Rossi and A. Perico, *J. Chem. Phys.*, **53**, 1223 (1970).

5) H. Benoit and P. M. Doty, *J. Phys. Chem.*, **57**, 958 (1953).

6) S. Arichi, M. Matsuura, Y. Yamamoto, and H. Murata *Bull. Chem. Soc. Jpn.*, **39**, 434 (1966).

7) A. Dondos and H. Benoit, *Macromolecules*, **4**, 279 (1971).

8) Y. Hirai and T. Yanagida, *Bull. Chem. Soc. Jpn.*, **51**, 2421 (1978).

9) M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolym. Forsch.*, **3**, 196 (1963).