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On The Structure-Dilute Solution Properties Relationship in Substituted Acrylamide Polymers

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ON THE STRUCTURE-DILUTE SOLUTION PROPERTIES RELATIONSHIP IN SUBSTITUTED ACRYLAMIDE POLYMERS

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ABSTRACT

Poly (N,o- methylphenylacrylamide) (PNOMPA) is prepared and fractionated by precipitation method. The fractions were characterized by viscometry, osmometry and gel permeation chromatography. The MHKS parameters were compared with other two polymers of the same class: poly (N-phenyl acrylamlide) (PNPA) and Poly (N, p-methylphenylacrylamide) (PNPMPA). The order of chain flexibility is found to be : PNOMPA > PNPMPA > PNPA. The cause for this is attributed to the decrease in hydrogen bonding by para and ortho methyl substitution. Further, the unperturbed dimensions of PNOMPA were worked out using Flory, Fox and schaefgen relation.

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INTRODUCTION

Industrial importance of substituted acrylamide polymers is well known but the studies on the solution behaviour of the phenyl substituted derivatives are meager. An earlier communication reports the molecular agregation phenomenon in poly (N- phenylacrylamide (PNPA)[1]. A methyl substitution to the phenyl ring of PNPA is expected to stiffen its backbone. The stiffness was, however, found [1] to decrease in case of p-methyl substitution. With a view to further investigating this effect, an o-methyl substitution was carried out to the PNPA backbone by the earlier procedure. The Mark-Howink-Kuhn-Sakurada (MHKS) constants and the flexibility parameters of this polymer as derived from the viscosity-molecular weight data of its fractions suggest a further decrease in the stiffness of the backbone. These results are summarized in this communication.

EXPERIMENTAL

The procedures for the preparation of N-O-methylphenylacrylamide (NOMPA) and its polymer PNOMPA were essentially the same as reported earlier [1] for other two polymers of this series. Fractional precipitation of the polymer was carried out using MEK/formamide system at 30 ± 0.1°C. The fractions were dried in vacuum at 45°C. A series of fractions with decreasing viscocity were obtained. Some of the fractions were refractionated using same solvent/non-solvent system in order to obtain homogeneity. Intrinsic viscosities of the fractions were measured in MEK by a suspended level Ubbelohde viscometer of zero shear rate. A Hewlett Packard 502 high speed membrane Osmometer was used for obtaining the number average molecular weights of the fractions. Molecular weight distributions were obained on a Waters Assc.-200 gel permeation chromatograph. The results are listed in Table 1.

RESULTS AND DISCUSSION

The heterogeneity data of PNOMPA (Table 1) does not show any evidence of macromolecular clustering as was observed [1] in case of PNPA. However following the note of caution envisaged earlier [1] number average molecular weights are used to derive MHKS relationship and other molecular charac-

TABLE 1

Intrinsic Viscosity, Molecular Weight and Polydispersity Data of PNOMPA Fractions

Fractions	$[\eta]$. dl/ g [a]	$\overline{M}_n \times 10^{-4}$ [b]	$\overline{M}_w/\overline{M}_n$ (gpc) [c]
PNOMPA-1	1.31	21.10	3.26
PNOMPA-2	1.06	6.74	2.60
PNOMPA-3	0.70	4.43	2.37
PNOMPA-4	0.66	3.52	2.07
PNOMPA-6	0.51	1.76	1.81
PNOMPA-7	0.46	1.51	1.89

a. $[\eta]$ in MEK at 30°C

b. Osmometry in MEK at 27° C; RT = 3.17×10^4 cm

c. Fraction 1 not included in the analysis due to high polydispersity.

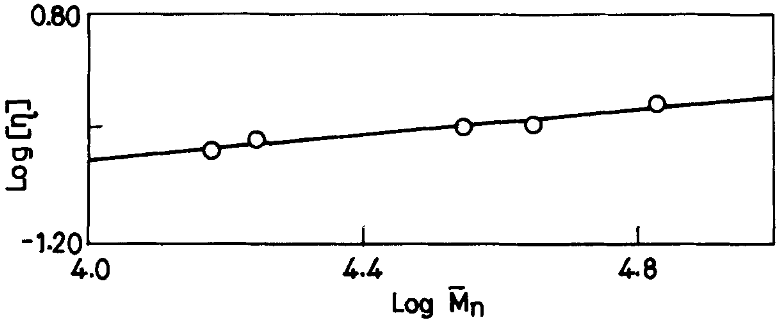

Figure 1. Plot of log $[\eta]$ versus log $\overline{M}_n$ of PNOMPA fractions

teristics. Figure 1 shows the MHKS plot based on the data of Table 1. The $[\eta]-M$ relation in MEK at 30° C comes out as :

$$[\eta] = 2.09 \times 10^{-3}\, \overline{M}_n^{0.55} \qquad (1)$$

The value of $\nu (= 0.55)$ in this case is found to be lesser than that of PNPA and PNPMPA reported earlier. This indicates that both PNPMPA and PNOMPA assume coiled conformation in solution. Methyl substitution in the phenyl ring of phenylacrylamide polymer is expected to stiffen its backbone. The MHKS exponent of PNOMPA when compared with PNPA and PNPMPA [1], however conflict this expectation The IR data of the polymers and the NMR data of the corresponding monomers regarding the lowering of carbonyl frequency and increase in the chemical shift of -N-H proton, respectively, showed the order of the extent of hydrogen bonding as :

PNPA > PNPMPA > PNOMPA

The introduction of methyl group due to its tendency to donate electrons, lowers the hydrogen bonding capicity of the amide group (-N-) in PNPMPA. As a result its chain becomes flexible in comparison to PNPA bringing the value of ν well below unity [1].The hydrogen bonding is further diminished in PNOMPA wherein methyl group occupies ortho position resulting into enormous steric hindrance.

Extending the scope of this analysis the $[\eta]$-M data of Table 1 was used to determine other molecular characteristics by constructing Flory, Fox and Schaefgen (FFS) plot due to the following equation [2], [3] :

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + 0.858\, K_\theta^{2/3}\, \Phi_0\, B(M/[\eta]) \qquad (2)$$

With $$K_\theta = \Phi_0\, q\, (<R^2>_0/M)^{3/2} \qquad (3)$$

Where $<R^2>_0$ is the unperturbed mean square end to end distance of polymer chains of molecular weight M, Φ_0 $(=2.87 \times 10^{21})$ is Flory's universal constant, and q is heterogeneity correction factor, to be calculated in the present case as :

$$q = q_n = \Gamma(h + 1.5)/h^{1/2}\, \Gamma(h+1) \qquad (4)$$

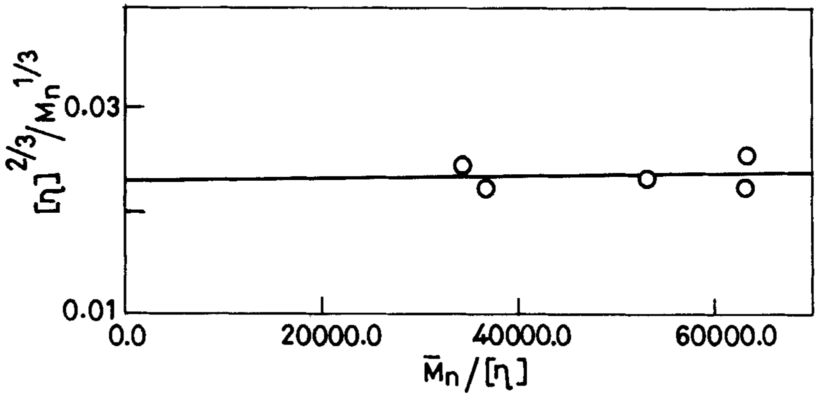

Figure 2. FFS plot of $[\eta]^{2/3} / \overline{M}_n^{1/3}$ versus $\overline{M}_n / [\eta]$

Figure 2 is constructed according to Equation 2 between $[\eta]^{2/3}/M^{1/3}$ vs. $M/[\eta]$ from the data of Table 1. The value of K_θ as derived from the intercept comes out to be 3.48×10^{-3} dl. mole$^{1/2}$. g$^{-3/2}$. Calculating the value of q (= 1.42) from the heterogeneity data of Table 1 and substituting in Equation 3, the unperturbed dimensions, $<R^2>_0 / M$ of PNOMPA in MEK at 30°C are calculated as : 9.48×10^{-1} Å . A detailed report on the determination of other configurational parameters and their comparison with relevant polymers will be published later.

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