

Chloromethylated Polystyrene in Dilute Solution

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SUMMARY

The macromolecular chain conformation of chloromethylated polystyrene and the effect of excluded volume have been studied by light scattering measurements.

INTRODUCTION

The aim of this paper is the study of chloromethylated polystyrene, by the light scattering and viscosimetry techniques, as well as its features in dilute solutions of benzene. The experimental measurements concerning the characteristic features of the macromolecular chain were discussed accordingly to the two parameter theory of the flexible polymers in solution.

EXPERIMENTAL

Materials

Chloromethylated polystyrene (CMPS) was prepared by chloromethylation of atactic polystyrene ($\bar{M}_w = 80,000$) in the presence of a Friedel - Crafts catalyst ($ZnCl_2$) (1). In order to avoid secondary reactions a large molar ratio of monochlordimethylether / styrene (about 36 : 1) was used. CMPS was carefully purified by solving it in dioxane and pouring it in methanol. The purified polymer contains 23 % Cl. By 1H -NMR spectra it has been established that $-CH_2Cl$ groups are predominantly in para position.

Benzene used as solvent for the viscosimetry and light scattering measurements was dried on sodium wire and previously distilled.

Methods

The fractionation of CMPS was performed by

the fractional precipitation of the polymer using methanol as nonsolvent. The initial concentration of the CMPS solution was of 0.9 g polymer in 100 ml solvent. The fractionation of polymer was carried out at 25°C, but solution was homogeneized at 40°C. The polymer fractions were carefully purified by precipitation with methanol and samples were vacuum dried at room temperature.

The polydispersity of the polymeric fractions was evaluated from the ratio $\overline{M}_w/\overline{M}_n$ determined by GPC, the average value was of 1.4.

Measurements of the intrinsic viscosity were performed on polymer solutions in benzene ($c \approx 2$ g/100 ml) using a Ubbelohde suspended-level viscosimeter at 25°C.

The light scattering measurements were performed on a P.C.L. Peaker apparatus using the following conditions : temperature, 25°C, wave length, 4360 Å, and angular domain of 40 - 140° (with an experimental precision + 6 %). The sample were filtrated through a sintered-glass filtre of G-5 porosity. The weight average molecular weights, the second virial coefficient and gyration radius were evaluated from Zimm's plot.

The refractive index increments were measured with a Zeiss interferometer at the same temperature and wave length (with an experimental precision of + 1.5 %).

RESULTS AND DISCUSSION

The weight average molecular weight (\overline{M}_w), the second virial coefficient (A_2) and the intrinsic viscosity ($[\eta]$), used to determine the short and long range molecular interactions are shown in Table 1.

Table 1. Light scattering and viscosimetry data

Sample	\overline{M}_w	$A_2 \times 10^4$ ($\text{cm}^3 \text{mol/g}^2$)	$[\eta]$.(ml/g)	$(\overline{r}^2)^{1/2}$ (Å)
1	579065	1.195	46.0	258
2	440000	1.267	39.0	218
3	200000	1.492	26.0	139
4	120000	1.751	19.0	105
5	77000	1.972	15.0	82
6	36000	2.684	10.0	54

From the Mark-Houwink's plot it was established the relationship between molecular weight and intrinsic

sic viscosity :

$$[\eta] = 3.168 \times 10^{-2} \bar{M}_w^{0.55} \quad (1)$$

The exponent of relation (1) suggests the flexibility of the macromolecular chain.

The conformation of the macromolecular chain
and the effect of the excluded volume

It is well known that A_2 and the expansion factor are depended of two parameters. One of them, β , is determined by the long range interactions between the segments which do not belong to the same chain and the second one, s_0^2/N (s_0^2 - mean square gyration radius in unperturbed state, N - number of the bonds), is a parameter related to the short range molecular interactions and it depends on the interactions between neighbored localized segments, along the macromolecular chain.

Theses short and long range interactions were evaluated from the experimental data (Table 1) by means of the equations (2-4) :

$$\frac{[\eta]}{M^{1/2}} = K + 0.51 \phi_0 B M^{1/2} \quad (2)$$

$$A_2 M^{1/2} = \psi_\infty A^3 + 0.631 \psi_\infty B M^{1/2} \quad (3)$$

where : $K = \phi_0 (\bar{L}_0^2/M)^{3/2}$; $A = (\bar{L}_0^2/M)^{1/2}$, the term $(\bar{L}_0^2)^{1/2}$ being the mean root square distance between the chain-ends in the unperturbed state ;

$\psi_\infty = 1.518 \times 10^{23} \text{ mole}^{-1}$; $\phi_0 = 2.87 \times 10^{21}$ and $B = \beta/m^2$ is the parameter of long range interaction which characterizes the chain expansion (m - molar weight of the monomer unit).

The conformation parameter values and the excluded volume of CMPS are listed in Table 2.

The sterical parameter (σ), which measures the hindrance of the free rotation around the carbon-carbon simple bond, due to the molar volume of the substituents in the main chain as well as the short range interactions between the chain units is defined by the ratio :

$\sigma^2 = \bar{L}_0^2 / L_{of}^2$, were L_{of}^2 is the unperturbed mean square end-to-end distance assuming a free rotation around the C-C bond.

$(\overline{L}_0^2)^{1/2}$ values were calculated by means of the equation (2) and (3) while \overline{L}_{of}^2 using the relationship: $(\overline{L}_{of}^2 / P) = 9.471 \times 10^{-16} \text{ cm}^2$ (independently of substituent (5) ; P - is the polymerization degree).

Table 2. Conformation parameters and excluded volume

Function calculated	Light scattering data (eq.3)	Viscosimetry data (eq.2)
$A = (\overline{L}_0^2 / M)^{1/2} \times 10^{11} \text{ cm}$	612	580
σ	2.45	2.33
$B \times 10^{27}$	1.189	0.342
$\beta \times 10^{24}$	27.65	7.9

If the molecular weight of CMPS unit is taken into account ($m = 152.45$), $(\overline{L}_{of}^2 / M)^{1/2} = 249 \times 10^{-11} \text{ cm}$.

The obtained values for σ show a lower flexibility of CMPS (Table 2) comparatively with polystyrene for which $\sigma = 2.22$, due to chloromethyl groups that lead to a stiffening of the macromolecular chain.

The excluded volume effect will be discussed in connection with the quantities defined by the linear expansion factor (α_s - eq. 4) and the interpenetration function (Ψ - eq. 5) :

$$\alpha_s^2 = \overline{s}^2 / \overline{s}_0^2 \quad (4)$$

$$\Phi = A_2 M^2 / 4\pi^{3/2} N_a \overline{s}^{3/2} \quad (5)$$

where : \overline{s}^2 - perturbed mean square radius of gyration; N_a - Avogadro's number.

According to the two parameter theory of the polymer solutions (5), α_s and Ψ depend on the excluded volume parameter (Z), given by the relationship :

$$Z = (3 / 2 \pi)^{3/2} (B / A^3) M^{1/2} \quad (6)$$

where A and B are independently of M, and Z is proportional with $M^{1/2}$ for a homogeneous series of polymers

and a given solvent.

In order to check the theoretical assumptions (6) which show that in the case of linear flexible polymers α_s^5 is proportional asymptotic with Z , α_s and Z were calculated from the equations (4) and (6) respectively, using L_0^2 , A and B given by the equation (3). Figure 1 collects the data in the form of α_s^2 plotted against $Z^{2/5}$, also including literature data for the system polystyrene/benzene (7).

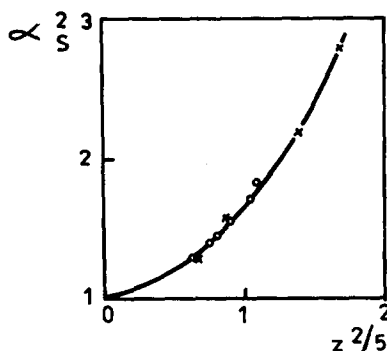


Fig. 1. A plot of α_s^2 versus $Z^{2/5}$: (o)- CMPS in benzene at 25°C (measured data); (x) - Polystyrene in benzene at 30°C (Fukuda and coworkers (7)).

The plotted points are approximately fitted by a single curve which is closely linear in the region where a majority of data points appear.

In order to prove the validity of the two parameter theory for the studied system it was investigated the dependence of Ψ on α_s^2 (Figure 2)

(8). The values were calculated from the measured data by means of the equations (4) and (5) respectively (curve 1). Curve (2) resulted by plotting of computed values according to the theoretical relationships (7) and (8) which take into account the inter- and intramolecular interactions (9).

In order to get α_s^2 from equation (8), the excluded volume parameter Z was estimated (eq. 6), using the values of parameters A and B included in Table 2 (column 2).

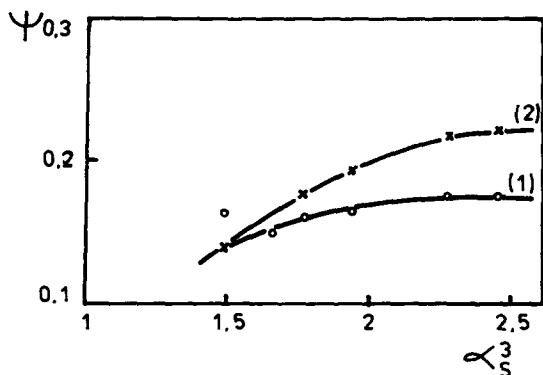


Fig. 2. A plot of Ψ versus α_s^3 : computed values according to:
 - curve 1 - relationships (4) and (5);
 - curve 2 - relationships (7) and (8)

$$\Psi = 0.547 [1 - (1 + 3.903 \bar{Z})^{-0.4683}] \quad (7)$$

(Kurata - Yamakawa)

$$\alpha_s^2 = 0.541 + 0.459 (1 + 6.04 Z)^{0.46} \quad (8)$$

(Yamakawa - Tanaka)

$$\text{where } \bar{Z} = Z / \alpha_s^3$$

From Figure 2 can notice for the molecular weight range searched in this work an increase of the polymer coil expansion due to the increase of excluded volume according to the two parameter theory for A_2 . The deviations from the theoretical curve are the larger the higher the molecular weight of the fractions. These deviations could be given by experimental errors, the polydispersity of the investigated fractions or the theoretical relationships chosen in this study.

Finally, it was tried to evaluate the Flory viscosimetric factor (ϕ) for this polymer-solvent system according to the equation (9):

$$\phi = \frac{[\eta] M}{6^{3/2} \alpha_s^{3/2}} \quad (9)$$

with s^2 determined by the light scattering.

From Table 3 one can observe that the Flory's factor decreases simultaneously with the increase of the coil expansion due to the excluded volume. For $\alpha_s = 1$, it was graphically determined $\phi = \phi_0 = 2.2 \times 10^{21}$ using the plot of $\phi = f(\alpha_s^3)$. This value is smaller than that theoretical one (2.87×10^{21}) found for the unperturbed polymer coil in a homogeneous series of molecular weights.

Table 3. Flory's viscosimetric factor

Sample	$\phi \times 10^{21}$	α_s^3
1	1.050	2.455
2	0.857	2.254
3	1.319	1.929
4	1.374	1.763
5	1.491	1.656
6	1.652	1.482

CONCLUSIONS

The parameters α and K of the Mark-Houwink's relationship were evaluated for the molecular weight range 30,000 - 600,000 using viscosimetry and light scattering measurements.

Calculation of the steric factor emphasizes a macromolecular chain stiffening of CMPS, comparatively with polystyrene due to the chloromethyl groups.

It was emphasized that the data in the form α_s^2 plotted against $Z^{2/5}$ are approximately fitted by a single curve. This remark offers further the possibility of the evaluation of the β binary cluster integral for a given system of polymer-solvent, by means of α_s (using relationships (6) and (7)).

By comparison of the theoretical and experimental results it was pointed out that the polymer coil expansion increases due to an excluded volume increase.

It was observed that the Flory's viscosimetric factor ϕ , decreases simultaneously with the polymer coil expansion increase due to the excluded volume increase.

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Received June 2, accepted June 4, 1982