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LIGHT SCATTERING FROM SOLUTIONS OF A SEMI-FLEXIBLE POLYMER AND A POLYELECTROLYTE BOTH HAVING SHARP MOLECULAR WEIGHT DISTRIBUTIONS

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The particle scattering factor in light scattering is determined for poly(tert-butyl crotonate) in n-butyl chloride and also for partially neutralized poly(acrylic acid) in aqueous solution in the presence of added neutral salt (NaBr). The former is a wormlike chain which is extended due to stiffness of the polymer chain, while the latter is extended due to the electrostatic repulsive force which is a kind of excluded volume effect. A clear difference is found between $P(\theta)$ of both polymers.

1. Introduction

In the θ solvent, not only non-ionic polymers but also polyelectrolytes have gaussian distributions of segments. (1) The intrinsic viscosity is proportional to the square root of molecular weight in both cases [1–3].

$$[\eta] = KM^{0.5} . \tag{1}$$

(2) The particle scattering factor in light scattering $P(\theta)$ agrees with the theory of Debye [4] in which the gaussian distribution of segments is assumed [5,6]

$$P(\theta) = 2u^{-2}[\exp(-u) - 1 + u] , \tag{2}$$

and

$$u = (16\pi^2/\lambda^2)\langle s^2\rangle_z \sin^2\theta/2 , \tag{3}$$

where $\langle s^2\rangle_z$ is the z-average mean-square radius of gyration of the polymer, λ is the wave length in the solvent, and θ is the scattering angle.

If the solvent power is increased, however, polymer chains expand into non-gaussian ones on account of the so-called excluded volume effect [1,7]. It is also well-known that the conformation of non-ionic linear polymers having stiff backbones, for example, DNA [8] and polyisocyanate [9] deviates from the gaussian chain and behaves like a wormlike chain [10,11]. The extended polymer due to the excluded volume effect must be different from wormlike chains, since the conformation of the polymer would more markedly deviate from the gaussian chain as the molecular weight increases, whereas the wormlike polymer should approach the gaussian chain as the molecular weight increases.

The difference in the distribution of segments in polymer can be most clearly studied by light scattering, that is, by observing the particle scattering factor $P(\theta)$ and comparing them with theories, if the polymer has a sharp molecular weight distribution. The calculation of $P(\theta)$ for wormlike chains was carried out by Sharp and Bloomfield [8] and by Yamakawa and Fujii [12] as follows:

$$P(\theta) = 2u^{-2}[\exp(-u) - 1 + u] + 4/(15L_r) + 7/(15uL_r) - [11/(15L_r) + 7/(15uL_r)] \exp(-u), \tag{4}$$

where

$$u = (16\pi^2/3\lambda^2)L(1/2\lambda')\sin^2\theta/2 , \tag{5}$$

$$L_r = \lambda' L , \tag{6}$$

and L is the contour length of polymer defined by

$$L = M/M_L , \tag{7}$$

where M_L is the molecular weight per unit length. $1/2\lambda'$ is called as persistence length and is related to the mean-square radius of gyration by

$$\langle s^2\rangle = (1/2\lambda')^2[2L_r/3 - 1 + 1/L_r - 1/(2L_r^2) + \exp(-2L_r)/(2L_r^2)] . \tag{8}$$

It is well-known that $P(\theta)$ in eq. (4) are well applicable to semiflexible chains [8,9].

$P(\theta)$ for the polymer coils extended by the excluded volume effect was given by Peterlin [13] such as

$$P(\theta) = \int_0^1 2(1-x)\exp(-u^{1+\epsilon})\mathrm{d}x \,, \tag{9}$$

and

$$u = (8\pi^2/3\lambda^2)(2+\epsilon)(3+\epsilon)\langle s^2\rangle \sin^2\theta/2 \,, \tag{10}$$

where the excluded volume effect parameter ϵ is defined by

$$\langle s^2\rangle = K'M^{1+\epsilon} \,. \tag{11}$$

At the θ state, ϵ is zero and increases as the solvent power is increased. The integration of eq. (9) was given by Ptitsyn [14] and Benoit [15] analytically, using incomplete gamma functions, and by Hyde et al. [16] numerically. Strictly speaking, ϵ is a parameter, but it must be close to the value estimated from the intrinsic viscosity molecular weight relationship versus

$$[\eta] = KM^a \,, \tag{12}$$

$$\epsilon = (2a-1)/3 \,. \tag{13}$$

Recent progress in the anionic polymerization technique allow us to have a semi-flexible chain, poly(tert-butyl crotonate) (PTBC) [17,18] and a polyelectrolyte, poly(acrylic acid) [19], (PAA), both having sharp molecular weight distributions. The exponents a of eq. (12) are larger than 0.5 for both polymers [17,20]. This fact implies that the conformations of both polymers deviate from the gaussian chain: PTBC may be a semi-flexible chain due to the steric hindrance between the methyl group at the β-position and the carboxyl group at the α-position [17]. If PAA is neutralized with an alkali, on the other hand, the molecule is extended by the electrostatic repulsive force which is usually assumed to be a kind of excluded volume effect. It is interesting to compare $P(\theta)$ of these two polymers.

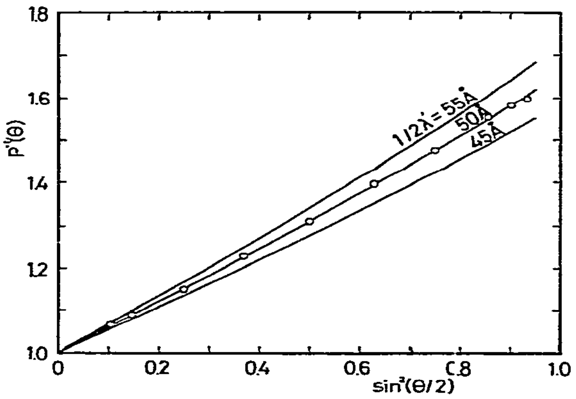

Fig. 1. Comparison of experimental $P(\theta)$ of PTBC in n-butyl chloride with the theory for wormlike chain, eq. (4), using $M_L = 60\,\text{Å}^{-1}$. The experimental $P(\theta)$ is denoted by open circles and the theoretical curves are shown by the solid line, using various values of $1/2\lambda'$.

2. Experimental

2.1. Samples

Preparation procedures of PTBC and PAA and their characterizations were reported in previous papers [17,18,19]. The molecular weights of PTBC and PAA are $3.5_1 \times 10^5$ and $1.5_0 \times 10^6$, respectively. Their molecular weight distributions have not been determined. But it is clear from their sedimentation patterns that their molecular weight distributions are narrow enough.

2.2. Light scattering

The reduced intensity of light scattered from polymer solutions is given by

$$KC/R_\theta = \frac{1}{M_w \cdot P(\theta)} + 2A_2C + \ldots \,, \tag{14}$$

and the optical constant K is

$$K = 2\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}C)^2/(N_A\lambda_0^4) \,, \tag{15}$$

where C is the concentration of polymer, R_θ is the Rayleigh ratio at the scattering angle θ, A_2 in the second virial coefficient, n_0 and n are the refractive indices of solvent and solution, respectively, N_A is Avogadro's number and λ_0 is the wave length *in vacuo*.

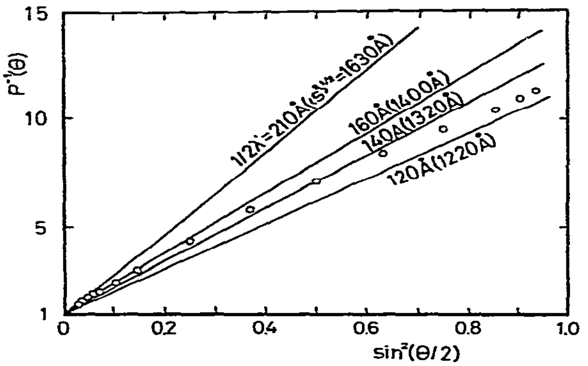

Fig. 2. Comparison of experimental $P(\theta)$ of partially neutralized PAA (degree of neutralization, $i = 0.6$) in 0.025 N NaBr aqueous solution with the theory for a wormlike chain, eq. (4), using $M_L = 40$ Å^{-1}. The values of $1/2\lambda'$ are shown in the figure. The values of $\langle s^2\rangle^{1/2}$ calculated from eq. (8), using $1/2\lambda'$ are also shown in the brackets.

Therefore, $P(\theta)$ can be experimentally determined by extrapolating (KCM_w/R_θ) to zero polymer concentration at various scattering angles.

$$\lim_{c\to 0}(KCM_w/R_\theta) = 1/P(\theta)\,. \tag{16}$$

The details in experiment will be reported elsewhere [6,21]. In the case of PAA, the sample solution is dialyzed against solvent.

3. Results

Fig. 1 shows the comparison between $P(\theta)$ of n-butyl chloride solution of PTBC with the theoretical curve of eq. (4), assuming a value for the persistence length $1/2\lambda'$ to have the best agreement between theory and experiments. Agreement between the theory theory and experiments is satisfactory if we assume $1/2\lambda' = 50$ Å. This value of $1/2\lambda'$ is in good agreement with the value which is chosen to have the best agreement between experimental hydrodynamic properties such as intrinsic viscosity, diffusion coefficient and theories [22].

Fig. 2 shows the comparison between $P(\theta)$ of partially neutralized PAA and the calculated values of eq. (4). It is impossible to have satisfactory agreement between eq. (4) and the experimental data by adjusting the persistence length $1/2\lambda'$. It is not impossible to reproduce the experimental results, it is required to assume *unreasonably* large values for $1/2\lambda'$ and M_L.

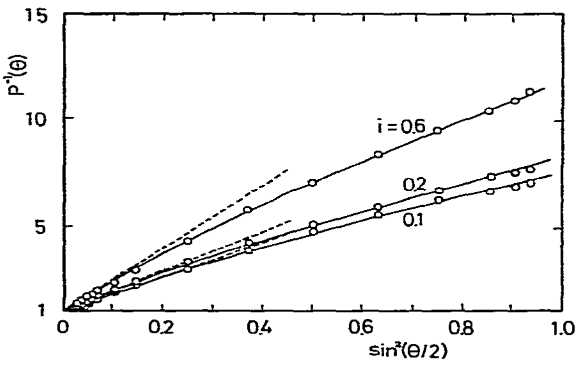

Fig. 3. Comparison of experimental $P(\theta)$ of partially neutralized PAA at various degree of neutralization, i, in 0.025 N NaBr aqueous solution with the theory of Peterlin, eq. (9). The solid lines are calculated, using $\langle s^2\rangle^{1/2} = 1630$ Å and $\epsilon = 0.30$ (0.24) at $i = 0.6$, $\langle s^2\rangle^{1/2} = 1300$ Å and $\epsilon = 0.25$ (0.23) at $i = 0.2$, and $\langle s^2\rangle^{1/2} = 1230$ Å and $\epsilon = 0.20$ (0.19) at $i = 0.1$. The values of ϵ in the brackets are estimated from eq. (13). Broken lines show the initial slope.

Fig. 3 shows the comparison of $P(\theta)$ of partially neutralized PAA with eq. (9). The values of ϵ are assumed to be nearly equal to the values calculated from eq. (13) using the $[\eta]$ data reported previously [20] and the values of $\langle s^2\rangle$ are chosen to have the best agreement between experimental $P(\theta)$ and calculated values of eq. (9). The values of $\langle s^2\rangle$ thus chosen are reasonable compared with the initial slopes in fig. 3. The initial slope gives $(16\pi^2/3\lambda^2)\langle s^2\rangle$ independently of the conformations assumed. The agreement between experimental and calculated values is quite satisfactory.

4. Discussion

The bending force constant a' for a continuous chain is related to the persistence length $1/2\lambda'$ by [23]

$$a'/kT = 1/2\lambda'\,, \tag{17}$$

where k is the Boltzmann constant and T is the absolute temperature. Since the bending force constant of a polyelectrolyte chain may be increased by the electrostatic repulsive force, it may seem reasonable to assume that polyelectrolytes extended by electrostatic repulsive force could be treated as wormlike chains. In practice, the intrinsic viscosity versus molecular weight relationship of polyelectrolytes can favourably be compared with the theory of intrinsic viscosity of wormlike polymers [6].

However, it is clear from the above experimental data that there is a clear difference in the distribution of segments between in a wormlike polymer extended due to stiffness of the polymer chain and in a polymer extended due to the excluded volume effect, although the intrinsic viscosity versus molecular weight relationships for both polymers deviate from eq. (1) in the same manner.

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