Spatial crossover for polyacrylamide in aqueous solution

R. Duplessix, M. Duval, J. François and D. Sarazin
Centre de Recherches sur les Macromolécules, CNRS, 6 rue Boussingault 67083 Strasbourg Cédex, France
(Received 4 November 1980)

Recent theories[1,2] have introduced the blob concept, which is related to a critical segment number N_c, required for the development of the excluded volume statistics. The confirmation of the crossover has been limited to the case of polystyrene–cyclohexane near θ conditions[3]. The results of a conformational study of well-defined polyacrylamide fractions of high molecule weight[4-7] have been interpreted on a blob theory basis, in terms of a particularly high value of N_c. The corresponding critical molecular weight M_c has been found to be 3×10^4, compared with 6×10^3 generally considered for polystyrene–benzene.

Thus the polyacrylamide–water systems seems to be well adapted for easy characterization of the conformational crossover. The order of magnitude of N_c suggests investigation by neutron scattering experiments since this technique is the only one which allows access to a **q** vector range (**q**, scattering vector) compatible with the value of radius of gyration to be measured.

For molecular weights lower than 3×10^4, we expect to find Gaussian behaviour with molecular dimensions (R_g) comparable with those determined for the high molecular weight range in a θ solvent.

Three fractions of a polyacrylamide (PASD10) were synthesized in our laboratory by radical polymerization. The details of the preparation and characterization of these samples will be reported elsewhere[8]. The molecular weights, M_w, were measured by light scattering using Fica apparatus and are listed in *Table 1*. The polydispersity indices have been evaluated by g.p.c. experiment[8].

Neutron scattering measurements were performed on the Institut Laue–Langevin D17 spectrometer, Grenoble[9]. The **q** vector range used covered the 10^{-2}–10^{-1} Å^{-1} domain: [$\mathbf{q}=(4\pi/\lambda)\sin(\theta/2)$, where λ = wavelength and θ = scattering angle]. Four concentrations (0.75%, 1%, 1.25%, 2%) of protonated polyacrylamide in D_2O, 0.1 N KBr solutions were used for each fraction.

The dimensions, given in *Table 1*, are obtained by extrapolation to zero concentration in a Zimm plot of scattered intensity. *Figure 1* shows one such plot, which does not reveal any aggregation or charge[10] effects.

The molecular weight dependence of the radius of gyration in the high molecular weight range had been found to be:

$$R_G = 0.0749 M_w^{0.64} \quad \text{(aqueous solutions)} \qquad (1)$$

Table 1

Sample	Molecular weight M_W	Radius of gyration R_G (Å)	Polydispersity index
PASD10 Z7	12600	48	<1.2
PASD10 Z6	16800	52	<1.2
PASD10 Z5	23500	58	<1.2

and

$$R_G = 0.390\ M_w^{0.5} \quad (\theta \text{ conditions; water–methanol mixture}) \qquad (2)$$

The logarithmic representation of these two scaling laws is shown in *Figure 2*, together with the values obtained in this work. It is evident that these new values are in rather good agreement with the Gaussian law while they cannot, in any way, fit the exluded volume behaviour.

Despite the small number of points, the preliminary experiment provides confirmation of the previous hypothesis concerning a high value of N_c for polyacrylamide in water. The same conclusions come out in a systematic study of viscometric behaviour, in a more extended range of molecular weights[8] ($10^4 < M_w < 3 \times 10^5$).

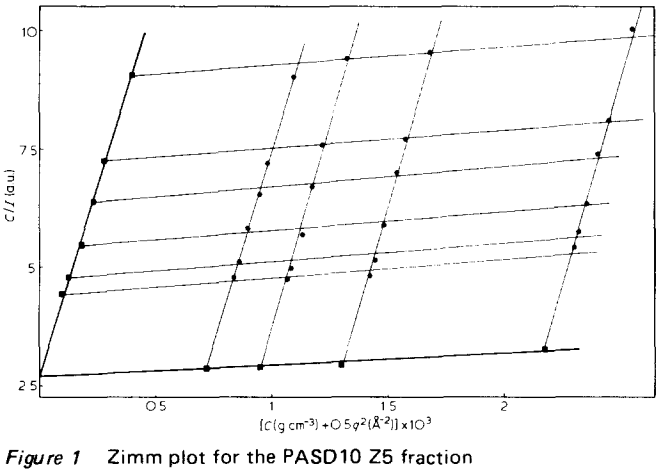

Figure 1 Zimm plot for the PASD10 Z5 fraction

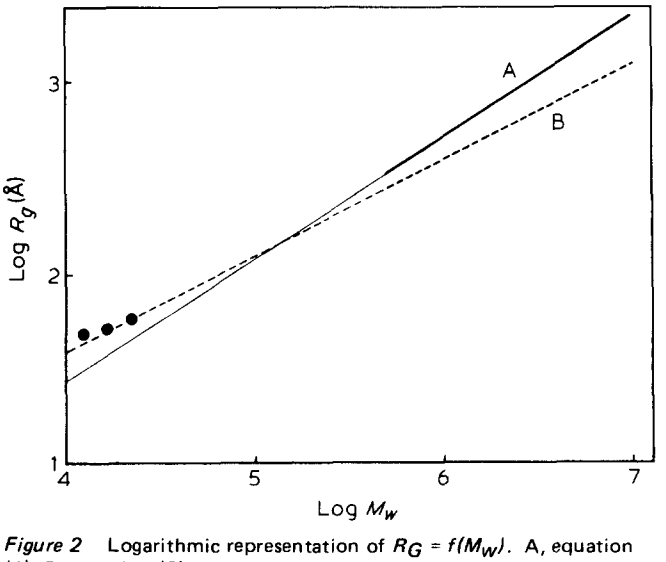

Figure 2 Logarithmic representation of $R_G = f(M_W)$. A, equation (1); B, equation (2)

0032-3861/81/030287-02$02.00

Moreover, further investigations of the **q** dependence of the scattered intensity in the intermediate **q** range should confirm this spatial crossover.

REFERENCES

1 de Gennes, P. G. 'Scaling Concepts in Polymer Physics' Cornell University Press, Ithaca, NY, 1979
2 Weill, G. and Des Cloizeaux, J. *J. Phys. (Orsay, Fr.)* 1979, **40**, 99
3 Farnoux, B. *et al. J. Phys. (Orsay, Fr.)* 1978, **39**, 77
4 Francois, J., Sarazin, D., Schwartz, T. and Weill, G. *Polymer* 1979, **20**, 969
5 Schwartz, T., Francois, J. and Weill, G. *Polymer* 1980, **21**, 247
6 Schwartz, T., Sabbadin, J. and Francois, J. *Polymer* 1981, **22**, in press
7 Francois, J., Schwartz, T. and Weill, G. *Macromolecules* 1980, **13**, 564
8 Duval, M., Sarazin, D. and Francois, J. *Polymer* in press
9 Neutron Beam Facilities at the HFR, Institut Max von Laue–Paul Langevin BP 156 X, 38042 Grenoble Cedex, France
10 Nierlich, M. *et al. J. Phys. (Orsay, Fr.)* 1979, **40**, 701

Proton spin–lattice and spin–spin relaxation in vinyl polymers in dilute solution: poly(methyl acrylate)

Frank Heatley and Michael K. Cox*

Chemistry Department, University of Manchester, Manchester, M13 9PL, UK

(*Received* 31 *October* 1980)

Introduction

^{1}H nuclear magnetic relaxation studies of poly(vinyl acetate)[1,2], polystyrene[3,4] and syndiotactic[5] and isotactic[6] poly(methyl methacrylate) have been reported previously, using a variety of techniques to probe molecular motions at widely different frequencies. The techniques included spin–lattice relaxation experiments using non-selective[1-6] and selective[4,6] inversion, spin–lattice relaxation with decoupling[1-3] and spin–spin relaxation[5,6]. Measurements have also been made at different resonance frequencies[2,4-6]. This paper describes an investigation of the spin–lattice and spin–spin relaxation of the backbone protons of poly(methyl acrylate) in dilute solution in $[^2H]_8$–toluene. The study was carried out with two objectives, firstly to extend the range of vinyl polymer structures studied in detail using ^{1}H relaxation, and secondly to examine the application to $[AX_2]_n$ spin systems of spin–spin relaxation measurements previously confined to $[A_2]_n^5$ or $[AX]_n^6$ systems.

Experimental

Relaxation measurements were performed at 300 MHz using a Varian Associates SC-300 spectrometer and at 80 MHz using a Bruker Spectrospin WP-80 spectrometer. Spin–lattice relaxation times were measured using the $(\pi-\tau-\pi/2)$ sequence and spin–spin relaxation times using the Carr–Purcell–Meiboom–Gill spin–echo sequence as described for syndiotactic poly(methyl methacrylate)[5] with a π pulse spacing of 1 ms. Experimental errors are approximately $\pm 5\%$.

The poly(methyl acrylate) was a sample with $M_w \sim 170000$ and $M_w/M_n \sim 2.2$, supplied by the Aldrich Chemical Company, Gillingham, UK. The n.m.r. spectrum showed it to be essentially atactic. The polymer was purified by precipitation from chloroform solution using diethyl ether and drying under vacuum. Measurements were made on a 1% (w/w) solution in $[^2H]_8$–toluene, degassed and sealed *in vacuo*.

Results

^{1}H chemical shifts of atactic (free-radical initiated) poly(methyl acrylate) in benzene solution have been determined[7] using partly deuterated polymers. The backbone methine proton (labelled *A*) resonates at 2.61δ. The backbone methylene protons (labelled *X*) in isotactic dyads are non-equivalent, resonating at 2.12 and 1.63δ, while the equivalent methylene protons in syndiotactic dyads resonate at 1.84δ. In the protonated polymers reported here, the peaks are broadened by spin–spin coupling which prevented resolution of the isotactic and syndiotactic *X* resonances at 80 MHz but not at 300 MHz. There was little dependence of the relaxation times on stereochemistry, and the *X* relaxation data reported here are an average over the two dyad types. Because of the overall width of the *X* resonance (150 Hz), it was impossible to saturate this signal without seriously perturbing the *A* signal. It was not practicable, therefore, to study *A* relaxation with *X* decoupling. However, the *A* signal was much narrower, so *X* relaxation with *A* saturated could be monitored.

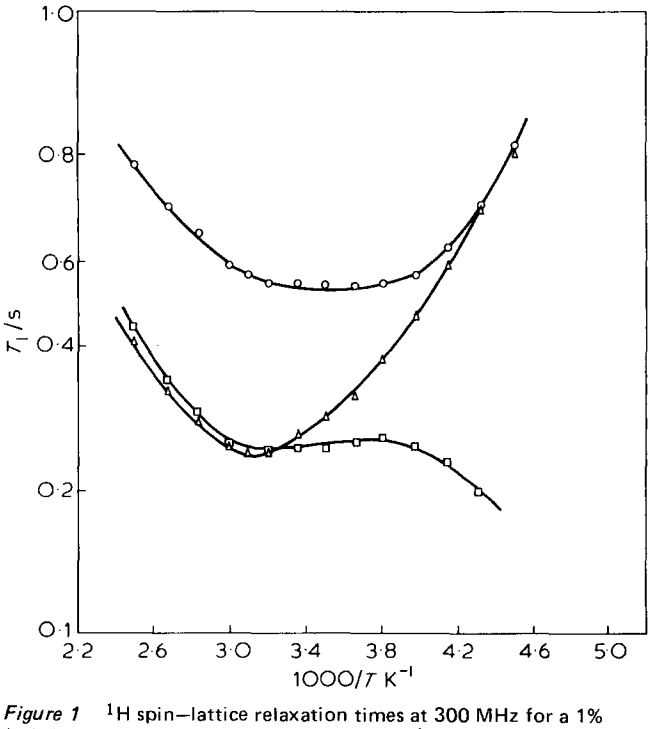

Figure 1 ^{1}H spin–lattice relaxation times at 300 MHz for a 1% (w/w) solution of poly(methyl acrylate) in $[^2H]_8$–toluene. ○, T_{1A}; △, T_{1X}; □, T_{XX}

* Present address: ICI Plastics Division, Welwyn Garden City, Herts, UK.

0032-3861/81/030288-03$02.00