Temperature-induced conformational transitions for flexible synthetic polymers in solution

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Herein we report experimental results on a wide variety of common, linear flexible polymers in solution in an attempt to confirm prior reports of abrupt 'conformational transitions' for these materials. Such transitions have been claimed by numerous authors, and they have been reported to reflect sudden conformational changes brought about, in most cases, by varying temperature. Methods used both in our work and earlier work include viscometry, differential refractometry and size exclusion chromatography. We observed no evidence of such conformational transitions and conclude that in reality such events are probably rare. We believe that many prior reports of such sudden changes in shape/size are probably mistaken because of the failure of some authors to take into account realistic experimental errors during data analysis and interpretation.

(Keywords: linear flexible polymers; conformational transitions; viscometry)

INTRODUCTION

To a large extent, the unique properties of polymers are a consequence of the potential for macromolecules to adopt a vast range of conformations. Thus, the molecules in an elastomer may be perturbed from their equilibrium random coil conformations by an applied stress, resulting in the individual molecular chains becoming more elongated. Upon removal of the applied force, the molecules again assume coil-like shapes.

Conformational changes are also extremely important for macromolecules in solution. Globular proteins are biopolymers of great importance, owing to their function as enzymes[1]. Biological activity is lost, however, if the protein is in its random coil (denatured) conformation.

For relatively stiff chain polymers, helix–coil transitions are well known[2–5]. Much experimental work has recently been devoted to studies of the 'coil–globule' transition for flexible polymers under very poor solvent conditions[6–11]. It has become increasingly apparent that while much contraction of flexible coils can occur under subtheta conditions, measurements on truly globular particles have probably never been reported for thermodynamically stable solutions[12,13].

In 1961 Reiss and Benoit[14] reported a strong conformational transition for isotactic polystyrene (PS) in solution at 80°C. Other workers have also observed irregular and much weaker variations of properties, including chain dimensions, with temperature for solutions of this polymer[15], although at lower temperatures. Roots *et al.*[16] found the hydrodynamic radius of isotactic PS in toluene to be virtually independent of temperature over the range 20–70°C. These results[16] are in strong contrast to the findings of Reiss and Benoit[14] who reported a ca. 25% increase in the radius of gyration for an isotactic PS in toluene over the same temperature range. Roots *et al.*[16] did, however, observe a transition at 55°C that they associated with changes in conformation and flexibility on a semilocal scale by neutron spin-echo spectroscopy. Since isotactic PS crystallizes in solution at temperatures below 80°C, yielding a polymer with a melting point of 80°C[17], 'unusual' property variations for such unstable solutions are not surprising.

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Since 1970 a great number of studies have appeared which report conformational transitions for solutions of common amorphous polymers in the vicinity of room temperature[18–45]. In the majority of cases the reported transitions were detected via intrinsic viscosity measurements, where discontinuities were observed as a function of temperature in single solvents (usually) or solvent composition in binary mixed solvents. Despite the widespread reports of these transitions, the underlying physical basis for such a phenomenon has not been elucidated. In fact, the classic book by Flory[46] on conformational properties of polymer chains does not consider the potential for dramatic conformational changes with temperature. Instead, changes in temperature are believed to impart gradual shifts in the Boltzmann equilibrium describing the relative populations of low energy rotational isomeric states (RISs)[46]. Although conformational transitions had been reported for poly(methyl methacrylate) (PMMA) in numerous solvents[18,20,22,23,30,32,34,36,37] prior to 1986, Vacatello and Flory[47], in reporting a highly refined six-state RIS model for PMMA, failed to make any mention of such transitions. Could it be that they considered such transitions for PMMA as 'non-events' based on theoretical grounds?

Motivated by this observation (and our combined experience with solutions of flexible polymers wherein we have never observed such transitions), we decided to reinvestigate the reported conformational transitions for several common macromolecules. Herein viscometry results are reported for PS in cyclohexane; poly(t-butylstyrene) (PtBS) in toluene; anionically produced PMMA in methyl isobutyl ketone (MIBK), acetonitrile and in mixtures of cyclohexane and 1,4-dioxane; free radical produced PMMA in MIBK, ethyl acetate and butyl acetate; poly(phenyl methacrylate) (PPMA) in MIBK; and poly(n-butyl methacrylate) (PBMA) in methyl ethyl ketone (MEK), benzene, 1,4-dioxane and cyclohexane. Differential refractometry was also applied to anionically made PMMA in MIBK and to PtBS in toluene. Size exclusion chromatography (s.e.c.) measurements were conducted as a function of temperature for PtBS in toluene and tetrahydrofuran (THF) in an attempt to locate a reported conformational change.

EXPERIMENTAL

Polymers

Polystyrene (PS) standards having molecular weights of 23 000 and 90 000 (manufacturer's data) were obtained from Pressure Chemical Company. These materials were specified to have polydispersity ratios $\bar{M}_w/\bar{M}_n$ (where $\bar{M}_w$ is the weight-average and $\bar{M}_n$ is the number-average molecular weight) less than 1.06. Polydispersities and molecular weights were confirmed in our laboratories by size exclusion chromatography (s.e.c.). Anionically polymerized poly(methyl methacrylate) (PMMA) standards (78% racemic dyads) having nominal molecular weights of 27 000, 52 500, 63 900, 107 000 and 330 000 and $\bar{M}_w/\bar{M}_n \leq 1.1$ were purchased from Pressure Chemical Company and Polymer Laboratories. Free radical produced poly(n-butyl methacrylate) (PBMA) and poly(phenyl methacrylate) (PPMA) were purchased from Aldrich Chemical Company. These materials were fractionated by standard solvent/non-solvent techniques involving the addition of methanol to dilute toluene solutions of the polymer. Characteristics of the selected PBMA and PPMA are presented in *Table 1*.

Table 1 Molecular characteristics of PBMA and PPMA fractions

Sample	$10^{-5}\bar{M}_w$[a]	$10^{-5}\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$
PBMA			
F-3	1.84	1.60	1.15[c]
F-6	3.67	2.96	1.24[c]
F-5	5.02	3.72	1.35[c]
PPMA			
F-1	4.15		1.30[d]
F-2	1.88		1.40[d]
F-3	1.04		1.30[d]
F-4	0.89		1.42[d]

[a] From light scattering
[b] From membrane osmometry
[c] From absolute measurements
[d] From s.e.c.

Poly(t-butylstyrene) specimens were prepared by anionic polymerization techniques as previously described[48,49]. The characteristics of the two polymers used in this work were $\bar{M}_w = 175\,000$ ($\bar{M}_w/\bar{M}_n = 1.08$) and $\bar{M}_w = 659\,000$ ($\bar{M}_w/\bar{M}_n = 1.17$). Fractions of free radical produced PMMA (78% racemic dyads) were obtained and characterized as described earlier[50]. The specimens used in this work had $\bar{M}_w = 469\,000$, $\bar{M}_w/\bar{M}_n = 1.34$; $\bar{M}_w = 223\,000$, $\bar{M}_w/\bar{M}_n = 1.23$; $\bar{M}_w = 186\,000$, $\bar{M}_w/\bar{M}_n = 1.16$; and $\bar{M}_w = 39\,000$, $\bar{M}_w/\bar{M}_n = 1.28$.

Solvents

1,4-Dioxane was obtained from Aldrich Chemical Company, refluxed over sodium and distilled and stored under nitrogen. Acetonitrile, cyclohexane, methanol, MEK, butyl acetate, ethyl acetate and chloroform were purchased from Aldrich in high performance liquid chromatography (h.p.l.c.) grade and used as received. Benzene, toluene and MIBK were obtained from Fisher Scientific Company in ACS Certified grade and were employed without further purification.

S.e.c.

Most of the s.e.c. measurements involved the use of a Waters model 510 pump and model 410 differential refractometer, with THF as the mobile phase at 1.0 ml min^{-1}. Two linear Ultrastyragel columns were used in series. S.e.c. measurements on PtBS as a function of temperature were conducted using a Waters 150C unit with a six-column Ultrastyragel set; toluene or THF at 1.0 ml min^{-1} served as the mobile phase.

Membrane osmometry

Membrane osmometry was utilized to measure the $\bar{M}_n$ of the PBMA fractions. A Mechrolab model 502 unit was employed at room temperature with toluene as the solvent. Data were analysed via square-root plots[51].

Differential refractometry

A Chromatix KMX-16 differential refractometer, having a laser light source operating at 633 nm wavelength, and an Otsuka Electronics DRM 1020 double-beam high sensitivity differential refractometer, capable of operating at various wavelengths, were employed for measurement of the refractive index increment d*n*/d*c*. Both instruments were calibrated using aqueous NaCl solutions. Solvents and solutions were filtered through

0.45 μm pore size filters directly into the cells. The Otsuka unit, which was temperature controlled using an external bath to $\pm 0.01^\circ$C, was used for measuring the variation of dn/dc with temperature. Four or more concentrations of polymer were used in each dn/dc determination (slope of Δn *versus c*).

Light scattering

Light-scattering determinations of $\bar{M}_w$ involved the use of Chromatix KMX-6 and Wyatt Technology Company DAWN-B laser light scattering units, as previously described[52,53].

Viscometry

Most viscometry experiments were performed manually using Ubbelohde dilution viscometers having solvent flow times greater than 120 s. Temperature was controlled to within $\pm 0.02^\circ$C using a water bath; manual timing was reproducible to ± 0.1 s. Charging of polymer solution and additions of pure solvent for dilutions were conducted gravimetrically. Four or five concentrations of polymer giving relative viscosities η_r between 1.1 and 1.4 were used to extract the intrinsic viscosity $[\eta]$ and Huggins coefficient k_H via the Huggins plot (reduced specific viscosity *versus c*). The Huggins plot is strictly linear[54] (correlation coefficient $\geqslant 0.998$) over this range of η_r. This eliminates the need to apply non-linear regression analyses, which can lead to large errors. Some work was also conducted using the Schott–Gerate AVS automated viscosity system. This unit combines automatic timing with superior temperature control ($\pm 0.01^\circ$C) to allow for accurate measurement of η_r values smaller than 1.1.

Digitization

In some instances it was necessary to acquire previously published experimental data from published figures, i.e. data were not provided in tabular form. For this work a Hitachi Tablet Digitizer, model HDG-12170, interfaced to a PC equipped with Autocad for windows, version 0.12, was used.

RESULTS AND DISCUSSION

Polystyrene

Dondos and coworkers[31,32] have reported a conformational transition at ca. 40°C for PS in cyclohexane. The transition was observed as a discontinuity in $[\eta]$ as a function of temperature with values measured at 40°C actually being smaller than values measured at the theta temperature (34.5°C). Since numerous studies on chain dimensions for PS in theta solvents as a function of temperature have appeared which show no evidence of such a transition[6,7,55–62], we decided to conduct our own intrinsic viscosity measurements on this system. It should be noted that while Tsitsilianis and Dondos[39] have claimed that the work of Tanaka *et al.*[6,7,62] on PS in cyclohexane supports their findings[31,32], no such evidence is apparent on examining the literature. Instead, the Tanaka group reported a rapid contraction of high molecular weight PS in cyclohexane below the theta temperature (coil–globule transition).

Our results for PS in cyclohexane are shown in *Table 2* and *Figure 1a*. As is clear upon examining *Figure 1a*, no conformational transition is apparent in our data over the entire range of temperature investigated. Likewise, no sharp changes in k_H are observed (*Table 2*), with the values gradually decreasing as temperature is increased. We believe the k_H values to be accurate to $\pm 10\%$ as opposed to $\pm 2\%$ for $[\eta]$. These errors are based on replicate analyses of the same sample in our laboratories[54,63]. Clearly, the $[\eta]$ results are preferred over k_H results in probing for conformational changes in macromolecules because of the smaller errors associated with the former measurements.

Table 2 Values of $[\eta]$ and k_H for polystyrene in cyclohexane at various temperatures

Temperature (°C)	$\bar{M}_w = 23\,000$ $[\eta]$ (dl g^{-1})	k_H	$\bar{M}_w = 90\,000$ $[\eta]$ (dl g^{-1})	k_H
30	0.131	0.69	0.237	0.69
32	0.136	0.86	0.245	0.70
34	0.144	0.63	0.243	0.64
36	0.143	0.68	0.252	0.57
38	0.147	0.65	0.256	0.55
40	0.153	0.47	0.257	0.64
42	0.155	0.50	0.262	0.55
44	0.155	0.58	0.263	0.59
46	0.156	0.49	0.264	0.57
48	0.158	0.52	0.272	0.50
50	0.160	0.55	0.276	0.50

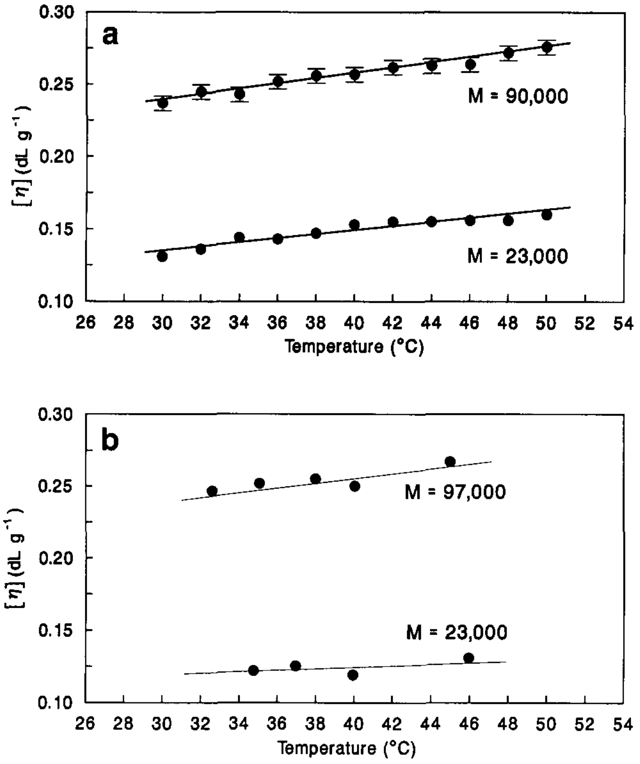

Figure 1 (a) Our data showing the variation of $[\eta]$ with temperature for PS in cyclohexane. For the sample with $M = 23\,000$, the size of the symbols corresponds approximately to the estimated error of $\pm 2\%$. (b) Results of Dondos *et al.*[31] for PS in cyclohexane

The results of Dondos *et al.*[31] are shown in *Figure 1b*. These data were obtained by digitization of data from the literature[31]. Correlation coefficients for our data fitted to a linear regression analysis are -0.9767 for $M = 90\,000$ and 0.9575 for $M = 23\,000$. These correlation coefficients can be compared with values of 0.8834 and 0.9951 for $M = 97\,000$ and $M = 23\,000$, respectively, for data from

Table 3 Values of $[\eta]$ and k_H for PtBS in toluene at various temperatures

Temperature (°C)	$\bar{M}_w = 175\,000$		$\bar{M}_w = 659\,000$	
	$[\eta]$ (dl g^{-1})	k_H	$[\eta]$ (dl g^{-1})	k_H
15	0.475	0.36	1.27	0.31
20	0.478	0.34	1.29	0.30
22	0.480	0.33		
25	0.474	0.38	1.25	0.34
27	0.481	0.33		
27.5			1.28	0.32
30	0.471	0.37	1.30	0.32
32.5			1.26	0.33
35	0.472	0.37	1.26	0.32
40	0.474	0.36	1.26	0.33

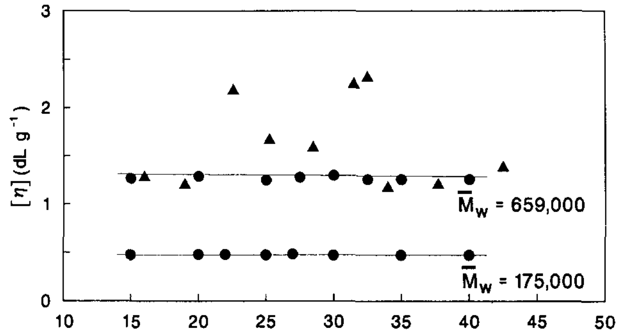

Figure 2 Variation of $[\eta]$ with temperature for PtBS in toluene. The circles correspond to our data which are fitted to straight lines with slopes of approximately zero. The triangles correspond to the data of Al-Ghezawi *et al.*[42] for a sample with a molecular weight of 180000

the literature[31]. Theory anticipates linear variations of $[\eta]$ with temperature over small intervals of temperature. Clearly all of these data sets are well fitted by a linear model.

It is clear on close inspection of *Figure 1b* that data points generated by Dondos *et al.*[31] at ca. 40°C consistently fall below the lines (or smooth curves) fitted to the other data. This leads us to suspect that a determinant experimental error not detected by the authors has caused these intrinsic viscosities to be underestimated. For example, if solvent viscosities used in determining $[\eta]$ values at 40°C were overestimated, $[\eta]$ values determined at this temperature would be consistently underestimated. If the authors intended firmly to establish lower $[\eta]$ values at 40°C, more experimental points at or near that temperature should have been obtained.

Poly(t-butylstyrene)

Very recently, Al-Ghezawi *et al.*[42] reported conformational transitions for PtBS in the good solvents toluene and cyclohexane. Their findings were based on both $[\eta]$ and d*n*/d*c* measurements as a function of temperature; discontinuities in the range 20–35°C were reported[42].

In *Table 3* and *Figure 2* we present viscosity data on PtBS in toluene as a function of temperature. The data for the sample with $\bar{M}_w = 175\,000$ have been previously reported[49]. Neither $[\eta]$ nor k_H data show any unusual variation with temperature. The sample with $\bar{M}_w = 175\,000$ was chosen so that the results could be directly compared with those obtained for a sample of nearly identical $\bar{M}_w$ by Al-Ghezawi *et al.*[42]; these data are also plotted in *Figure 2*. Whereas we find $[\eta] = 0.476 \pm 0.004$ dl g^{-1} (the error is the standard deviation), Al-Ghezawi *et al.*[42] report values ranging from about 1.1 to 2.4 dl g^{-1} for a sample of the same molecular weight. Our $[\eta]$ value in toluene for the $\bar{M}_w = 175\,000$ sample is virtually identical to that measured for the same sample in the other good solvents benzene and cyclohexane[49]. For the $\bar{M}_w = 659\,000$ sample we obtain $[\eta] = 1.27 \pm 0.017$ dl g^{-1}, again showing that $[\eta]$ does not vary with temperature.

Clearly, there are huge differences between our data and those of Al-Ghezawi *et al.* for PtBS with $\bar{M}_w = 175\,000$. Interestingly, if either our data or those of Al-Ghezawi *et al.* are fitted to linear regressions, slopes of virtually zero are obtained. However, the sum of squared residuals for the linear regression fit to our data is 8.57×10^{-5}, whereas the sum of squared residuals for the data of Al-Ghezawi *et al.* is 1.87. This huge difference, we believe, reflects strong random scatter in their data from experimental errors. For example, the presence of dust in solutions used in capillary viscometry experiments is known[54] to lead to scatter in data obtained and also to larger apparent $[\eta]$ values.

We were at a loss to explain these discrepancies, and therefore we measured both the peak elution volume (V_p) by s.e.c. and d*n*/d*c* as a function of temperature in toluene for the $\bar{M}_w = 175\,000$ specimen. These results are shown in *Table 4* and the d*n*/d*c* results are plotted in *Figure 3*. No variation is observed in peak elution volume over the range 25–40°C ($V_p = 44.0 \pm 0.05$ ml). Tsitsilianis and Dondos[39] have previously touted the use of s.e.c. for observing conformational transitions. A mild progressive increase is observed in d*n*/d*c* with increasing temperature (*Figure 3*); values range between 0.061 and 0.070 ml g^{-1}. We can routinely measure d*n*/d*c* to ± 0.002 ml g^{-1} using the Otsuka refractometer (based upon replicate analyses). Thus, the error bars in *Figure 3* represent experimental errors of $\pm 3\%$. In contrast to our findings, Al-Ghezawi *et al.*[42] report erratic and large variations in d*n*/d*c* for PtBS with $\bar{M}_w = 180\,000$ in toluene and cyclohexane over the same temperature range. For example, their d*n*/d*c* values in toluene for the $\bar{M}_w = 180\,000$ sample vary between 0.08 and 0.12 ml g^{-1} (much larger than our values shown in *Figure 3*). Conversely, their d*n*/d*c* results for PtBS with $\bar{M}_w = 6\,400\,000$ in toluene are in reasonable agreement with our results, taking into account their lower wavelength (436 nm). A further puzzle, however, is why extremely large (ca. 50%) d*n*/d*c* differences are noted

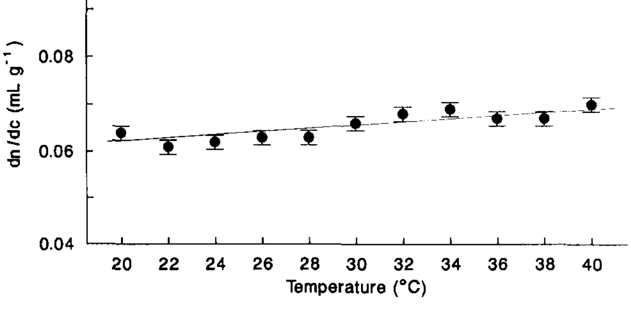

Figure 3 Dependence of d*n*/d*c* on temperature for PtBS in toluene. The error bars correspond to $\pm 3\%$

Table 4 S.e.c. peak elution volumes (V_p) and values of d*n*/d*c* for PtBS ($M = 175\,000$) in toluene at various temperatures

Temperature (°C)	V_p^a (ml)	d*n*/d*c*^{b} (ml g^{-1})
20		0.064
22		0.061
24		0.062
25	44.0	
26		0.063
27.5	43.95	
28		0.063
30	43.95	0.066
32		0.068
32.5	44.0	
34		0.069
35	44.0	
36		0.067
38		0.067
40	44.0	0.070

^{a} Peak elution volumes of 44.0±0.05 ml were also measured for this polymer in THF over the temperature range 25–40°C

^{b} At 488 nm

Table 5 Values of $[\eta]$ and k_H for PMMA (anionically produced) in MIBK and acetonitrile as a function of temperature

Temperature (°C)	PMMA $\bar{M}_w$	$[\eta]$ (dl g^{-1})	k_H
MIBK			
20	63 900	0.133	1.78
25	63 900	0.136	1.96
30	63 900	0.141	1.49
35	63 900	0.147	1.25
20	107 000	0.209	0.85
25	107 000	0.214	0.86
30	107 000	0.217	0.99
35	107 000	0.222	0.96
Acetonitrile			
40	52 500	0.118	1.71
45	52 500	0.123	1.32
47	52.500	0.123	1.44
48	52 500	0.122	1.49
49	52 500	0.119	1.91
50	52 500	0.121	1.33
52.5	52 500	0.125	1.37
55	52 500	0.125	1.42
40	107 000	0.176	1.09
45	107 000	0.179	1.12
47	107 000	0.176	1.13
48	107 000	0.177	1.43
49	107 000	0.177	1.57
50	107 000	0.189	0.96
52.5	107 000	0.189	1.13
55	107 000	0.190	1.26

in their work for the $\bar{M}_w = 180\,000$ *versus* $\bar{M}_w = 6\,400\,000$ PtBS samples in toluene[42]. Values of d*n*/d*c* are not expected to show any molecular weight dependence for samples of such high molecular weight.

Linear regression analysis of our d*n*/d*c* data (*Figure 3*) indicates a small positive slope, as expected, and the sum of squared residuals equals 2.35×10^{-5}. The d*n*/d*c* data of Al-Ghezawi *et al.* for the same system, which we obtained by digitization, also indicate a small positive slope, but the sum of squared residuals for these data is 9.05×10^{-4}. Notice the nearly two orders of magnitude difference in the totals of the squared residuals for data sets that are almost identical in size. Any data set with a large degree of scatter can be expected to exhibit apparent maxima or minima simply by chance. Again the authors[42] should have attempted to confirm the existence of the cited minimum by making additional measurements in the vicinity of the reported conformational transition.

Anionically produced PMMA

As noted in the Introduction, a great many studies have appeared which have suggested conformational transitions for PMMA in solution. Values of $[\eta]$ and k_H are collected in *Tables 5* and *6* for anionically made specimens in MIBK, acetonitrile and in mixtures of cyclohexane and dioxane. Examination of the PMMA/MIBK $[\eta]$ data (*Table 5*) clearly indicates only a gradual increase in $[\eta]$ with increasing temperature. This is expected, since MIBK is a poor solvent for PMMA. The k_H data show consistently larger values for the $\bar{M}_w = 63\,900$ sample *versus* the $\bar{M}_w = 107\,000$ sample. We have no explanation for this result; however, large k_H values have been noted for PMMA in other poor solvents[50]. The discontinuity reported by Katime *et al.*[37] for this system over the 25–30°C temperature range is not observed here. Similar results are noted for PMMA in acetonitrile (*Table 5* and *Figure 4*). Tsitsilianis and Dondos[32] reported a distinct drop in $[\eta]$ at 50°C for this system, as well as a large increase in k_H at the same temperature. We observe no such transition, although in our experience we feel that experimental errors are somewhat larger for this system than for others. Likewise, no transition is observed

Table 6 Values of $[\eta]$ and k_H for PMMA (anionically produced) in a mixture of cyclohexane and dioxane at 25°C as a function of solvent composition

Cyclohexane content (vol%)	PMMA $\bar{M}_w$	$[\eta]$ (dl g^{-1})	k_H
45	27 000	0.114	1.28
46	27 000	0.125	0.70
47	27 000	0.122	0.69
48	27 000	0.133	0.53
49	27 000	0.122	0.55
50	27 000	0.121	0.51
51	27 000	0.117	0.70
52	27 000	0.114	0.69
45	107 000	0.280	0.65
46	107 000	0.281	0.56
47	107 000	0.264	0.64
48	107 000	0.248	0.84
49	107 000	0.234	0.88
50	107 000	0.229	1.20
51	107 000	0.210	1.77

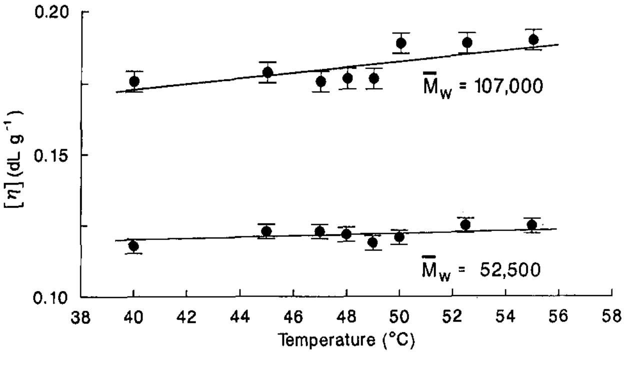

Figure 4 Variation of $[\eta]$ with temperature for anionically produced PMMA in acetonitrile. The error bars correspond to ±2%

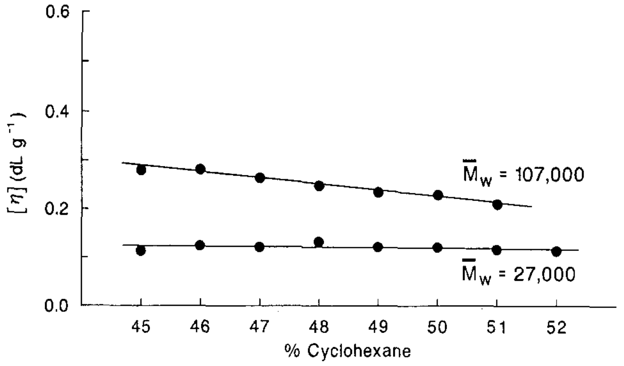

Figure 5 Dependence of [η] for anionically produced PMMA on solvent composition (by volume) for cyclohexane/dioxane mixtures

Table 7 Values of dn/dc (at 488 nm) as a function of temperature for anionic PMMA in MIBK

$\bar{M}_w = 63\,900$		$\bar{M}_w = 107\,000$	
Temperature (°C)	dn/dc (ml g^{-1})	Temperature (°C)	dn/dc (ml g^{-1})
20	0.096	40	0.099
25	0.096	43	0.100
30	0.097	45	0.103
35	0.099	48	0.103
38	0.100		
40	0.100		

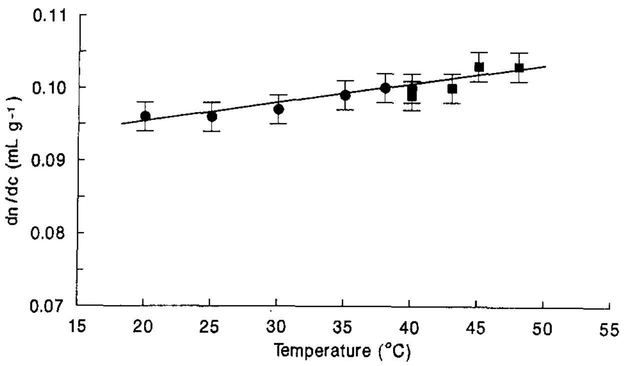

Figure 6 Dependence of dn/dc on temperature for anionic PMMA in MIBK: (●) $M = 63\,900$; (■) $M = 107\,000$. The error bars correspond to ±2%

at ca. 47–48% cyclohexane for PMMA in cyclohexane/dioxane mixtures (*Table 6* and *Figure 5*). Such an effect was previously reported by Tsitsilianis and Dondos[36].

Results for dn/dc of anionic PMMA in MIBK are summarized in *Table 7* and *Figure 6*. Only a slight, steady increase in dn/dc is observed as the temperature is increased from 20 to 48°C. The transition in the vicinity of 40–45°C reported for the PMMA/MIBK system by Katime *et al.*[37] is not seen in our work.

Free radical produced PMMA

Values of [η] and k_H for free radical produced PMMA in three solvents are given in *Tables 8* and *9*. The data for three different $\bar{M}_w$ materials in MIBK are plotted in *Figure 7*. Here it is apparent that no unusual variations occur in [η] over the studied temperature range, in contrast to the behaviour reported by Katime *et al.*[37]. Likewise, in *Figure 8a*, our data for PMMA in ethyl acetate and butyl acetate show no irregular behaviour. The increase in [η] with temperature for PMMA/butyl acetate is caused by increasing thermodynamic solvent quality as the temperature is increased, owing to the poor solvent character of butyl acetate for PMMA at room temperature. Likewise, a decrease in k_H with increasing temperature is observed (*Table 9*). In contrast to our findings, Katime *et al.*[22], using free radical produced PMMA, reported transitions centred around 50°C for both of these systems. They observed these transitions,

Table 8 Values of [η] and k_H for PMMA (free radical produced) in MIBK at various temperatures

Temperature (°C)	PMMA $\bar{M}_w$	[η] (dl g^{-1})	k_H
20	39 000	0.124	0.64
25	39 000	0.126	0.49
30	39 000	0.137	0.59
35	39 000	0.137	0.53
40	39 000	0.146	0.66
45	39 000	0.151	0.66
20	186 000	0.298	0.64
25	186 000	0.315	0.52
30	186 000	0.326	0.58
35	186 000	0.343	0.37
40	186 000	0.345	0.39
45	186 000	0.354	0.47
20	223 000	0.324	1.04
25	223 000	0.332	0.81
30	223 000	0.343	0.75
35	223 000	0.371	0.58
40	223 000	0.377	0.84
45	223 000	0.393	0.57

Table 9 Values of [η] and k_H for PMMA ($\bar{M}_w = 469\,000$) in ethyl acetate and butyl acetate at various temperatures

Temperature (°C)	Ethyl acetate		Butyl acetate	
	[η] (dl g^{-1})	k_H	[η] (dl g^{-1})	k_H
20	0.710	0.45	0.404	1.00
30	0.718	0.43	0.436	0.91
35	0.717	0.48	0.466	0.85
40	0.728	0.38	0.478	0.84
45	0.751	0.41	0.485	0.81
50	0.736	0.43	0.506	0.78
55	0.740	0.37	0.520	0.80
65	0.753	0.49	0.538	0.75

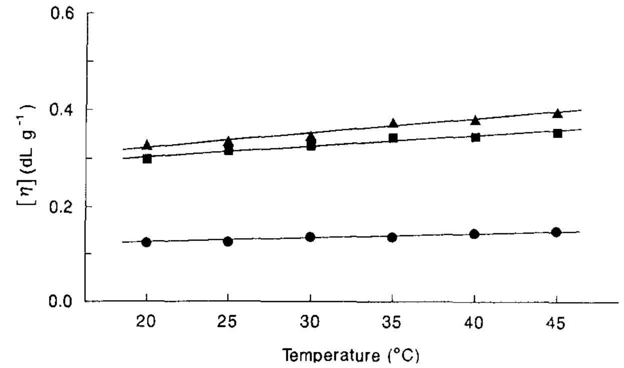

Figure 7 Variation of [η] with temperature for free radical produced PMMA: (●) $\bar{M}_w = 39\,000$; (■) $\bar{M}_w = 186\,000$; (▲) $\bar{M}_w = 223\,000$

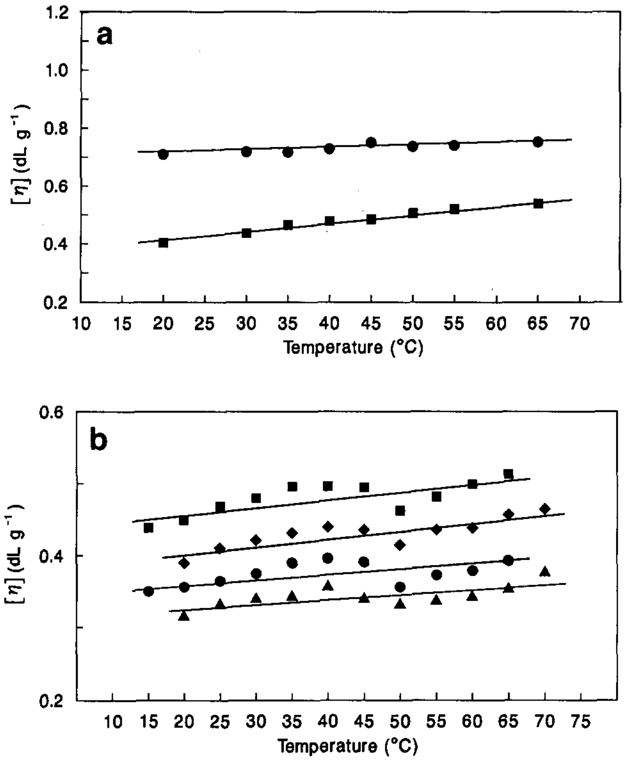

Figure 8 (a) Dependence of $[\eta]$ on temperature for free radical produced PMMA ($\bar{M}_w = 469\,000$) in ethyl acetate (●) and butyl acetate (■). (b) Data of Katime *et al.*[22] for PMMA in butyl acetate (▲, $\bar{M}_w = 325\,000$; ◆, $\bar{M}_w = 494\,000$) and ethyl acetate (●, $\bar{M}_w = 325\,000$; ■, $\bar{M}_w = 494\,000$)

Table 10 Values of $[\eta]$ and k_H for PPMA in MIBK

Temperature (°C)	PPMA $\bar{M}_w$	$[\eta]$ (dl g^{-1})	k_H
15	89 000	0.154	0.62
20	89 000	0.152	0.51
25	89 000	0.150	0.72
30	89 000	0.154	0.55
35	89 000	0.151	0.66
38	89 000	0.150	0.68
15	104 000	0.194	0.48
20	104 000	0.192	0.55
25	104 000	0.190	0.56
30	104 000	0.188	0.62
35	104 000	0.186	0.64
38	104 000	0.185	0.60
15	188 000	0.274	0.52
20	188 000	0.272	0.54
25	188 000	0.268	0.57
30	188 000	0.270	0.55
35	188 000	0.268	0.56
38	188 000	0.265	0.56
20	415 000	0.416	0.32
25	415 000	0.408	0.38
30	415 000	0.404	0.39
35	415 000	0.399	0.42

via viscosity measurements, for a series of different molecular weight fractions ranging from 325 000 to 2 000 000 in $\bar{M}_w$. Our sample has $\bar{M}_w = 469\,000$, so it lies within this range. To allow visual comparison of their data with ours, in *Figure 8b* we have plotted the data of Katime *et al.* for two PMMA samples having molecular weights of 325 000 and 494 000.

Not only do we fail to observe any conformational transition for PMMA, we also observe much larger $[\eta]$ values in both solvents for a sample with $\bar{M}_w = 469\,000$ than Katime *et al.* observe for their sample with $\bar{M}_w = 494\,000$ (*Figure 8*). The linearity of our data should be compared to the pronounced oscillatory nature of the data of Katime *et al.* While we cannot offer a definite explanation for these differences, we do note that our large k_H values in butyl acetate at the lowest temperatures strongly suggest poor to theta solvent conditions; solvent quality appears to increase as the temperature is increased (based on smaller k_H values). One should expect $[\eta]$ values to show a strong variation with temperature for polymer/poor solvent systems[64]. We observe such a variation for our butyl acetate data in *Figure 8*; the $[\eta]$ data of Katime *et al.* for PMMA in butyl acetate (*Figure 8*) show only a very weak temperature dependence. This latter result is inconsistent with theoretical expectations.

Poly(phenyl methacrylate)

A conformational transition over the temperature range 20–30°C has been reported for the PPMA/MIBK system by Katime and Garay[35]. Our viscometric results for this same system are recorded in *Table 10*. Both the polymers used in this and in the earlier work[13] were obtained by fractionation of a commercial (Aldrich), radical-polymerized sample. In our data (*Figure 9*), we observe only a very gradual decrease in $[\eta]$ as the temperature is increased. The k_H values for a given sample exhibit a correspondingly mild increase in magnitude, as expected, with increasing temperature. We observe nothing which could be interpreted as a sudden temperature-induced change in conformation.

Poly(n-butyl methacrylate)

Values of $[\eta]$ and k_H for PBMA in benzene, cyclohexane, 1,4-dioxane and MEK are presented in *Tables 11* and *12*. Benzene is a thermodynamically good solvent for PBMA, as evidenced by the larger $[\eta]$ values measured in this solvent and by the small constant k_H values typical of those for flexible linear chains in good solvents[65]. Statistical analysis of the $[\eta]$ data gives averages of 0.494 ($\pm$0.010), 0.761 ($\pm$0.011) and 0.965 ($\pm$0.012) dl g^{-1} for the $\bar{M}_w = 184\,000$, 367 000 and 502 000 samples, respectively. The cited errors correspond to standard deviations ranging from 1.2 to 2% for the three specimens. Clearly, the $[\eta]$ values are constant within experimental error and no unusual variations as a function of temperature are seen in either $[\eta]$ or k_H for this system. In contrast, Simionescu *et al.*[38] have reported 'discontinuities' in $[\eta]$ over the temperature range 25–35°C for solutions of

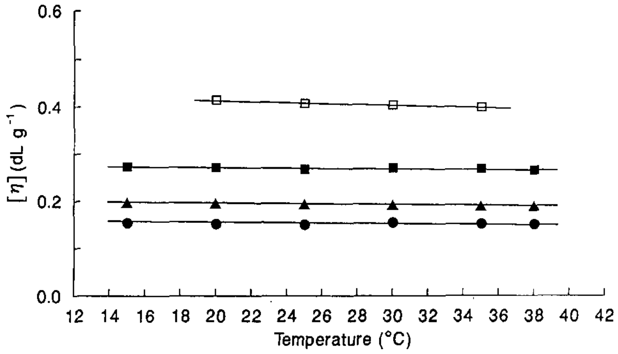

Figure 9 Variation of $[\eta]$ with temperature for PPMA in MIBK: (●) $\bar{M}_w = 89\,000$; (▲) $\bar{M}_w = 104\,000$; (■) $\bar{M}_w = 188\,000$; (□) $\bar{M}_w = 415\,000$

Table 11 Values of [η] and k_H for PBMA in benzene and cyclohexane

		Benzene		Cyclohexane	
Temperature (°C)	PBMA $\bar{M}_w$	[η] (dl g^{-1})	k_H	[η] (dl g^{-1})	k_H
15	184000	0.481	0.38	0.199	0.89
25	184000	0.491	0.35	0.248	0.63
30	184000	0.497	0.31	0.274	0.51
35	184000	0.493	0.34	0.296	0.43
45	184000	0.509	0.31	0.325	0.40
15	367000	0.753	0.30	0.267	1.15
25	367000	0.763	0.31	0.341	0.77
30	367000	0.750	0.29	0.391	0.61
35	367000	0.763	0.33	0.413	0.57
45	367000	0.777	0.29	0.488	0.47
15	502000	0.968	0.29	0.330	0.86
25	502000	0.961	0.30	0.425	0.63
30	502000	0.950	0.31	0.464	0.55
35	502000	0.964	0.30	0.502	0.50
45	502000	0.983	0.27	0.588	0.48

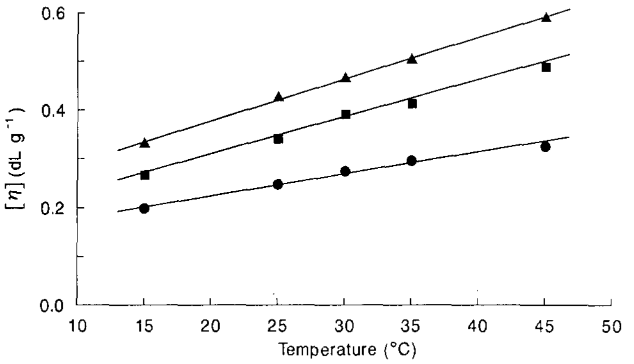

Figure 10 Dependence of [η] on temperature for PBMA in cyclohexane: (●) $\bar{M}_w = 184000$; (■) $\bar{M}_w = 367000$; (▲) $\bar{M}_w = 502000$

Table 12 Values of [η] and k_H for PBMA in 1,4-dioxane and MEK

		1,4-Dioxane		MEK	
Temperature (°C)	PBMA $\bar{M}_w$	[η] (dl g^{-1})	k_H	[η] (dl g^{-1})	k_H
15	184000	0.377	0.43		
25	184000	0.389	0.48		
35	184000	0.407	0.31		
45	184000	0.422	0.33		
15	367000	0.569	0.40	0.587	0.33
25	367000	0.579	0.42	0.586	0.32
35	367000	0.596	0.36	0.594	0.35
45	367000	0.618	0.36	0.592	0.35
15	502000	0.710	0.45		
25	502000	0.726	0.43		
35	502000	0.751	0.32		
45	502000	0.794	0.32		

PBMA in benzene, cyclohexane, 1,4-dioxane and MEK. We do not confirm their findings for benzene or the other solvents (see below).

Cyclohexane is a thermodynamically poor solvent for PBMA based on the small [η] values and large k_H values in *Table 11*. It becomes a progressively better solvent as the temperature is increased (*Figure 10*). Again, we see no indication of any conformational transition. Even more surprising is the fact that according to the [η] data presented in Figure 1 of the paper by Simionescu *et al.*[38], [η] values in cyclohexane should be equal to or larger than values of [η] measured in benzene at the same molecular weight. This is clearly not the case (see *Table 11*). 1,4-Dioxane and MEK are thermodynamically moderate solvents based on the [η] and k_H data of *Table 12* and become slightly better solvents for PBMA as the temperature is increased (*Table 12* and *Figures 11* and *12*). As before, no irregular variations of the type claimed by Simionescu *et al.*[38] are observed in our work.

CONCLUSIONS

We have re-examined many of the flexible synthetic polymer/solvent systems where conformational transitions have been reported. We have observed no evidence for such transitions in any of our work with many systems utilizing viscometry, differential refractometry and s.e.c. Clearly conformational transitions of various types do exist for many polymers[1–7]. However, they are not observed in our hands for the polymers studied which are flexible, amorphous, uncharged, of modest molecular weight and in solvents which range from poor to good in the thermodynamic sense. Conformational transitions of the type described in the literature[14–45] may possibly occur in some systems. Our experience suggests that such transitions are much less common than many papers appearing since 1970 would have us believe.

Finally, it is necessary to comment on recent claims by Dondos and coworkers[44,45] that conformational transitions can only be easily observed in solutions of synthetic polymers if extremely dilute solutions are used. These workers have defined a critical concentration c^{**}

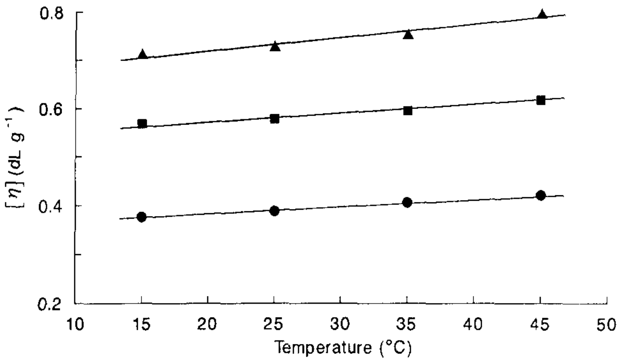

Figure 11 Dependence of [η] on temperature for PBMA in 1,4-dioxane (symbols as in *Figure 10*)

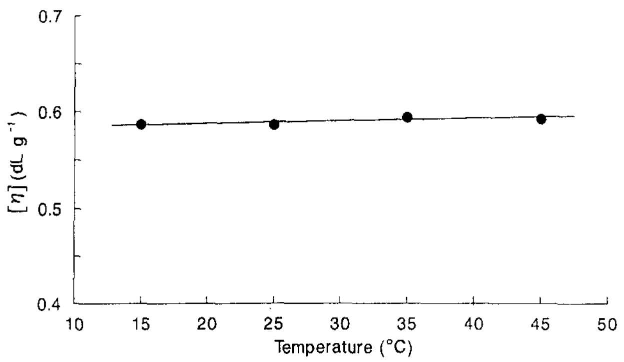

Figure 12 Variation of [η] with temperature for PBMA ($\bar{M}_w = 367000$) in MEK

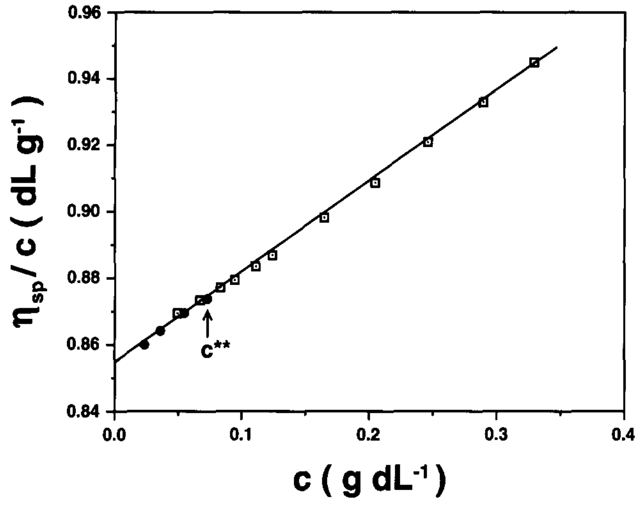

Figure 13 Reduced specific viscosity as a function of concentration for PS with $M=115000$ in 1,4-dioxane at 25°C. Different symbols correspond to separate stock solutions

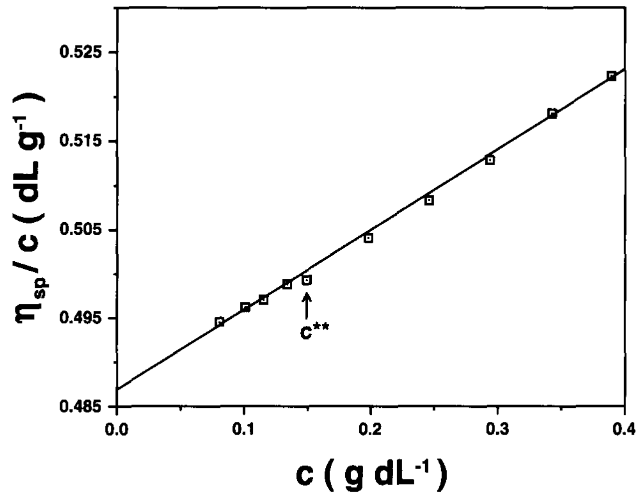

Figure 14 Reduced specific viscosity as a function of concentration for PS with $M=233000$ in 1,4-dioxane at 25°C

which reportedly separates extremely dilute solutions ($c<c^{**}$) from dilute solutions ($c>c^{**}$)[44,45]. This c^{**} presumably occurs at some concentration much lower than the well-established[66,67] overlap or critical concentration c^*, at which chains start to interact physically to a substantial degree. Above c^{**} the chain dimensions are reported to undergo a 'compression'[44,45], which may be detected as a downturn in a plot of reduced specific viscosity (η_{sp}/c) *versus* c.

We see no physical reason why any coil compression should occur below the well-established overlap concentration c^*. Furthermore, coil compressions of this type, i.e. this existence of c^{**}, have never been detected, to our knowledge, by direct scattering measurements. Scattering measurements are better suited to work at extremely low concentrations than are $[\eta]$ experiments. Nevertheless, we decided to examine the viscosity behaviour of two PS samples in 1,4-dioxane at 25°C. This is a system in which the c^{**} transition has been reported by Dondos and Tsitsilianis[44]. Two nearly monodisperse PS standards were used. One specimen was from Pressure Chemical Company, with $\bar{M}_w$ reported as 233000, and the other sample ($\bar{M}_w=115000$) was from Polymer Laboratories. The same high sensitivity, automated system for capillary viscometry used by Dondos and coworkers[44,45], the Schott-Gerate AVS system, was used in our work. We reproduced all flow times to ± 0.01 s. Furthermore, the concentrations used covered the same range as utilized by Dondos and Tsitsilianis[44] for PS specimens of $\bar{M}_w=115000$ and 216000 (virtually identical molecular weights to those used in our work). Our viscosity results for PS with $M=115000$ and $M=233000$ are presented in *Figures 13* and *14*, respectively. We observe a linear variation of η_{sp}/c with c; there is no indication of any downturn at lower concentrations as previously reported[44]. Thus, we can neither rationalize nor detect the reported c^{**} transition.

We are unable to reproduce the reported unusual behaviour for solutions of many synthetic polymers. Many prior attempts to support the occurrence of conformational transitions for flexible polymers in solution, we believe, are unconvincing because of a lack of adequate experimental care, a failure to consider realistic experimental errors and a failure to analyse adequate numbers of samples. The authors would be happy to cooperate with other groups in any future attempts to detect such transitions.

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