Conformational transition in syndiotactic PMMA: 6. Mono- and dichlorobenzene

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We have studied the thermal behaviour of syndiotactic PMMA in several solvents by viscometry. We have found a conformational change in the temperature range 293–308 K.

Keywords Conformational transition; solvent nature; self-association; steric hindrance; solvating power; umperturbed dimensions

INTRODUCTION

The first paper on conformational transitions in synthetic polymers was reported by Reiss and Benoit[1] in 1961. They found a sudden change in the mean square radius of gyration, $\langle s^2 \rangle$, at 80°C in the polystyrene/decaline system.

In previous papers[2–4] we have shown that atactic PMMA suffers a conformational transition in different solvents. We have also shown that the magnitude of ΔK_θ at the transition varies depending on the nature of the solvent[4]. Here we give the results obtained for several syndiotactic PMMA fractions in mono- and dichlorobenzenes (*ortho* and *meta* isomers) which show that tacticity is another parameter which greatly influences the appearance of the conformational transition in this polymer. In particular, we have found that the transition for syndiotactic PMMA occurs at lower temperatures than for the atactic polymer.

EXPERIMENTAL

All samples were obtained by anionic polymerization of methyl methacrylate at 203K[5]; its molecular weight distribution, determined by both light scattering and membrane osmometry, is relatively narrow ($\bar{M}_w/\bar{M}_n \simeq 1.17$).

Chlorobenzene, *o*-dichlorobenzene and *m*-dichlorobenzene were purified by standard procedures and freshly distilled before use.

A modified Ubbelohde suspended-level dilution viscometer was used[6]. The kinetic energy correction was less than 0.3% and, therefore, was neglected. The temperature of the water bath was regulated to ±0.05°C.

Determination of intrinsic viscosities (dl g^{-1}) was made by extrapolating plots of $\ln \eta_r/c$ and η_{sp}/c against concentration, respectively, to infinite dilution so that both plots gave the same intercept.

The number-average molecular weights, $\bar{M}_n$, of the polymers were measured in toluene solution with a Mechrolab 502 osmometer.

A FICA instrument was used. Benzene was used as a standard for calibration, using unpolarized light of wavelength 546 nm and taking the Rayleigh ratio at right angles to the incident beam[7] as 16.3×10^{-6} cm^{-1}. The solutions were purified by centrifuging in a preparative Sorwall at 15 000 rpm using an SS-34 rotor. Weight-average molecular weights were obtained by extrapolation of reduced scattering intensity values to zero concentration.

Steric composition was determined for all polymers from the n.m.r. spectra in deuterated chloroform, according to the method of Bovey and Tiers[8]. *Table 1* shows the characteristics of all the samples.

RESULTS AND DISCUSSION

Figure 1 shows the variation of $\ln[\eta]$ as a function of temperature for two samples studied in chlorobenzene, *o*-dichlorobenzene and *m*-dichlorobenzene. As can be seen, a sharp decrease of the intrinsic viscosity in a given temperature range, for all solvents and molecular weights studied, is observed. This indicates that the hydrodynamic volume of the polymer has decreased, and therefore its molecular dimensions have varied. The decrease can only be explained if we assume that PMMA has suffered a conformational change[9–12]. A smart and simple way of quantifying this phenomenon can be carried out by calculating the unperturbed dimensions of the polymer, $\langle s_0^2 \rangle / M$, using, for example, one of the excluded volume theories. The most commonly used theory, owing to both mathematical simplicity and the good results obtained, is the Stockmayer–Fixman one[13]:

Table 1 Characterization of samples of PMMA

			Steric composition		
Sample	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	i	s	h
PMMA-1	0.30	0.26	3	82	15
PMMA-2	1.14	0.99	2	81	17
PMMA-3	2.53	2.20	3	80	17
PMMA-4	4.10	3.60	2	80	18
PMMA-5	5.00	4.16	4	81	15
PMMA-6	6.90	5.80	2	82	16
PMMA-7	10.00	8.48	2	81	17

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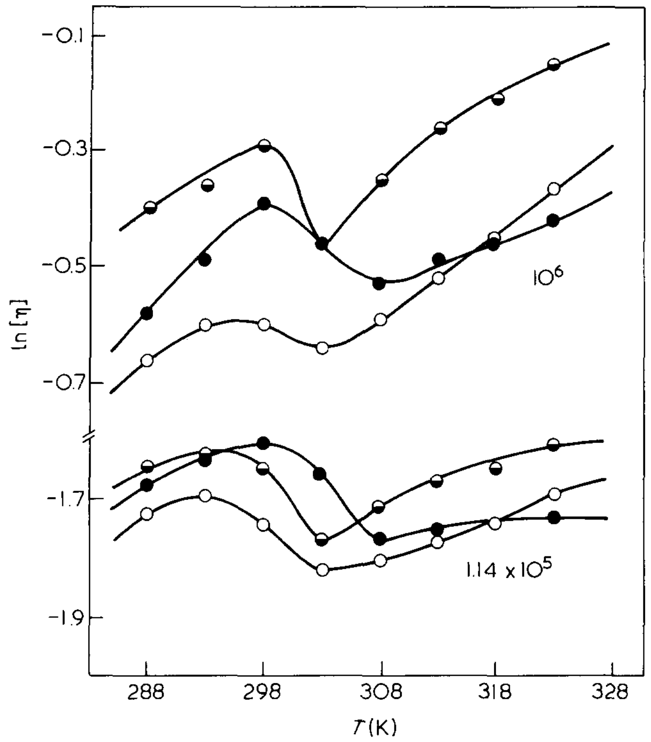

Figure 1 Variation with temperature of ln[η] for syndiotactic PMMA in chlorobenzene (◒), *o*-dichlorobenzene (○) and *m*-dichlorobenzene (●), for two different fractions identified by values of $\bar{M}_w$

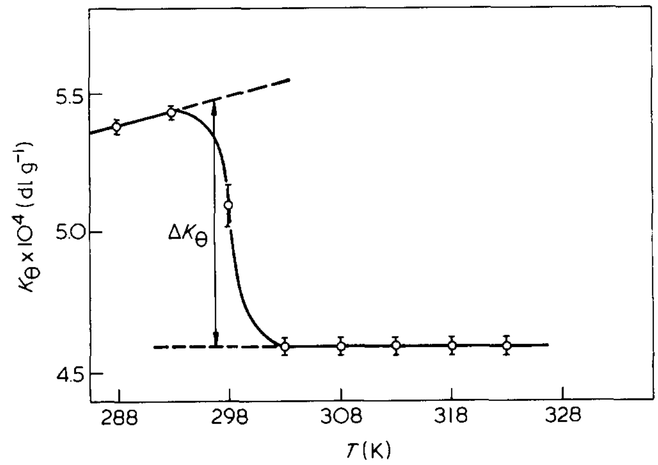

Figure 2 Variation of K_θ with temperature in chlorobenzene for syndiotactic PMMA

$$\frac{[\eta]}{M^{1/2}} = K_\theta + 0.51\Phi_0 B M^{1/2}$$

where B is a polymer–solvent interaction parameter and Φ_0 is the Flory constant.

In *Figures 2–4*, where we have plotted the variation of K_θ with temperature, a conformational change for the syndiotactic PMMA can be seen in all cases. However, the temperature range ΔT_t where the transition occurs is not always the same. Thus, for example, the conformational transition in chlorobenzene and *o*-dichlorobenzene can be observed between 20° and 30°C, while for *m*-dichlorobenzene it appears between 25° and 35°C. It is important to consider the fact that the variation of the unperturbed dimensions, ΔK_θ, is not always the same. Thus, for example, we have found that

$$\Delta K_\theta(o\text{-}C_6H_4Cl_2) < \Delta K_\theta(C_6H_5Cl) < \Delta K_\theta(m\text{-}C_6H_4Cl_2)$$

These differences can be attributed to the different solvating powers[14] of the solvents used, as can be deduced from the dipole moments of these solvents. In *Table 2* we give ΔK_θ, ΔB, dipole moments and K_θ before the conformational transition. As can be seen, when solvent polarity increases ΔK_θ decreases in the transition range. Dondos and Benoit[15] have explained the variation of K_θ in different solvents by supposing a liquid self-association which is a function of liquid polarity. The self-association increases with the dipole moment.

If we compare these results with those obtained elsewhere[16–19] we can see that ΔT_t is not the same for atactic PMMA. This can be attributed only to different steric compositions of the polymers used. This behaviour has been tested in isotactic PMMA, but no anomaly has been found in the temperature interval −5° to 50°C. In atatic PMMA we have found that the conformational transition is located at higher temperatures[16–19]. To explain this, it is necessary to take into account the experimental results obtained until now (K_θ decreases when conformational transition occurs; the conformational transition is reversible) which indicate that PMMA transitions with temperature are a consequence of *trans→gauche* changes[20]. The syndiotactic PMMA

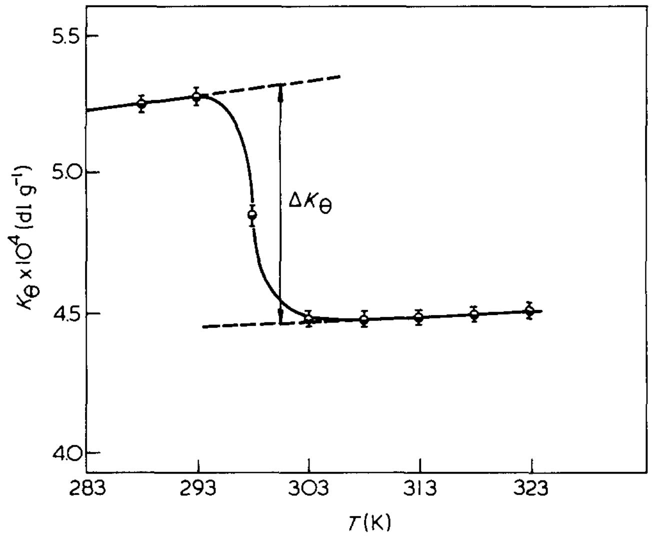

Figure 3 Variation of K_θ with temperature in *o*-dichlorobenzene for syndiotactic PMMA

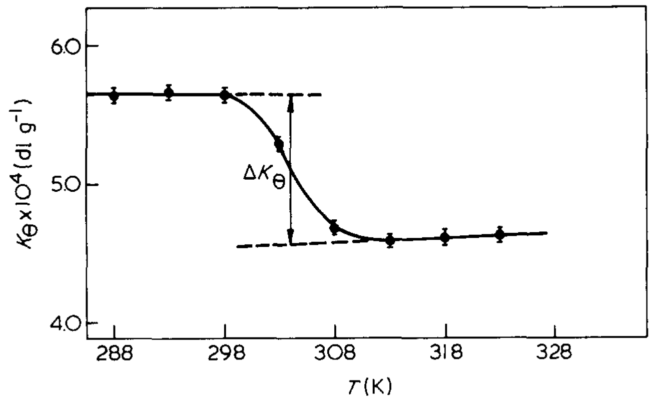

Figure 4 Variation of K_θ with temperature in *m*-dichlorobenzene for syndiotactic PMMA

Table 2 Solvent dipole moments, unperturbed dimensions before and after transition, ΔK_θ, and interaction parameter, ΔB, for syndiotactic PMMA in different solvents

Solvent	μ (D)	$K_\theta \times 10^4$ (dl g^{-1}) before	after	ΔK_θ (%)	ΔB (%)
m-Dichlorobenzene	1.37	5.65	4.58	19.9	50.0
Chlorobenzene	1.54	5.40	4.60	14.8	28.6
o-Dichlorobenzene	2.27	5.25	4.50	14.3	35.0

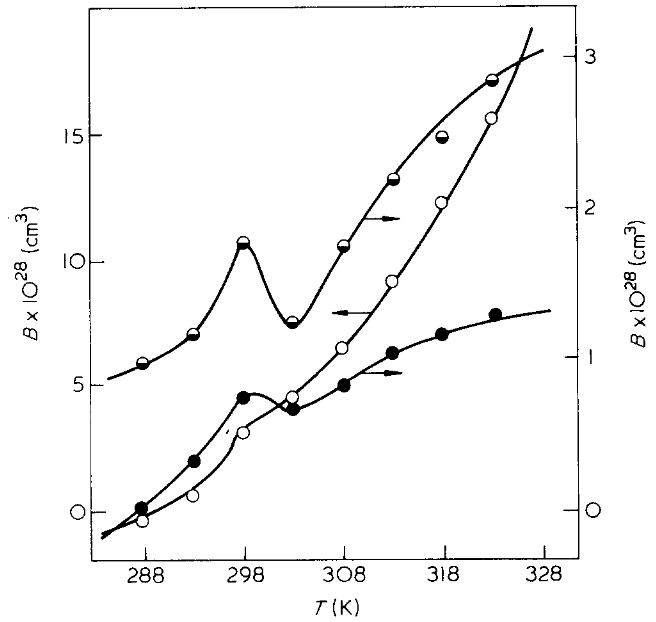

Figure 5 Plot of interaction parameter B against temperature for chlorobenzene (◒), *o*-dichlorobenzene (○) and *m*-dichlorobenzene (●)

conformation is more extended than that of atactic PMMA[21]. Thus, steric hindrance is lower in the syndiotactic polymer. Consequently, the energy (temperature) necessary to induce the transition will be lower in the syndiotactic form.

We have also evaluated C_∞ before and after the conformational transition. The values obtained, for the solvents employed here, range between 7.42 and 7.80, and 6.65 and 6.87, respectively. These values agree with those obtained by different authors[22-25]. This behaviour indicates that the steric hindrance has become lower when transition occurs.

Nevertheless, the great variation of interaction parameter in the transition is to be noted, ΔB, mainly for *o*- and *m*-dichlorobenzene (*Figure 5*). Spevacek and Schneider[26] have found that both syndio- and isotactic PMMA associate in *o*-dichlorobenzene. For this reason, it could be expected that a similar phenomenon occurs in *m*-dichlorobenzene. Besides, these authors[27] have pointed out that syndiotactic PMMA aggregates begin to disappear about 35°C, a temperature included in the range where the conformational transition occurs, while isotactic PMMA aggregates decompose at 160°C. These experimental results lead us to think that the sharp variations observed in K_θ and B for atactic and syndiotactic PMMA between 20° and 40°C may be due to either a conformational transition and/or rupture of intramolecular associates of PMMA. This supposition could explain the fact that for isotactic PMMA no anomalous behaviour has been found. At this moment we are investigating the contribution of both effects to the phenomenon.

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