Colloid Polym Sci (2003) 282: 84–87
DOI 10.1007/s00396-003-0944-8

SHORT COMMUNICATION

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Study of the conformational transition of polystyrene–poly(methyl methacrylate) block copolymers with temperature using measurements of the *c*** critical concentration

Received: 14 February 2003
Accepted: 26 March 2003

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Abstract The conformational transition of block copolymers has been studied until now using measurements of the second virial coefficient and the radius of gyration (light scattering) or of the intrinsic viscosity. In this paper the conformational transition of polystyrene–poly(methyl methacrylate) diblock copolymers with temperature is studied using measurements of the critical concentration *c*** which is obtained in the dynamic state (viscometry) and in the static state (UV measurements).

Keywords Block copolymer · Conformational transition · Concentration *c*** · Viscometry · UV

Introduction

The critical concentration *c*** which separates dilute solutions in extremely dilute solutions, $c < c^{**}$, and dilute solutions, $c > c^{**}$, has been studied experimentally in the dynamic and static states [1, 2, 3, 4, 5, 6]. This concentration is attributed to the appearance of the first entanglements between the macromolecular coils. These entanglements have been predicted theoretically by Brostow and Drewniak [7]. *c*** is in general 10 times lower than the well known critical overlapping concentration *c** and at *c*** the macromolecular coils do not occupy the entire volume of the solution.

It has been shown that *c*** is tightly related to the hydrodynamic volume of the coils of the macromolecules [1, 2, 3, 4, 5, 6, 8]. Any parameter affecting the hydrodynamic volume also affects the observed value of *c***, such as the molecular mass [1, 2, 3, 4, 5, 6], the shear rate [6], the quality of the solvent [2] and the molecular architecture [6]. More precisely, for a given polymer–solvent system, we obtain the same absolute value for the exponent in the power laws $\log[\eta]–\log M$ and $\log c^{**}–\log M$.

In this article we show that *c*** is capable of confirming the conformational transition of a block copolymer. Conformational transitions have already been observed by viscometry and light scattering for many block copolymers in a certain temperature region [9, 10, 11, 12].

More precisely, in the relatively narrow temperature region the block copolymer of polystyrene–poly(methyl methacrylate) (PS–PMMA) adopts a compressed

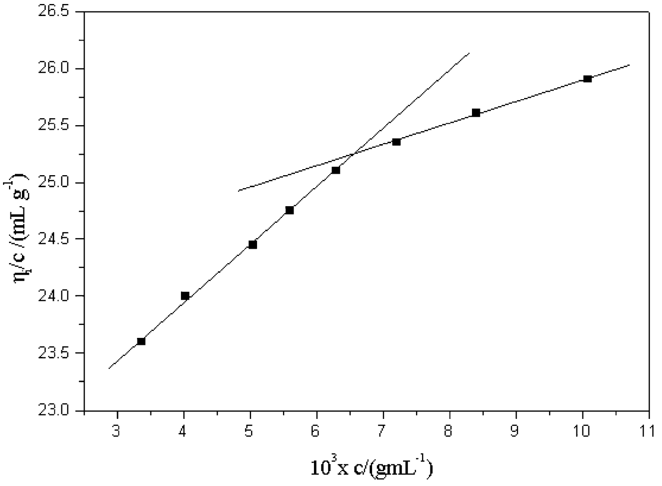

Fig. 1 Variation of the reduced viscosity as a function of the concentration of one fraction of polystyrene (*PS*) ($M_w = 20{,}000$) in chloroform ($c^{**} = 0.65$ g/100 ml)

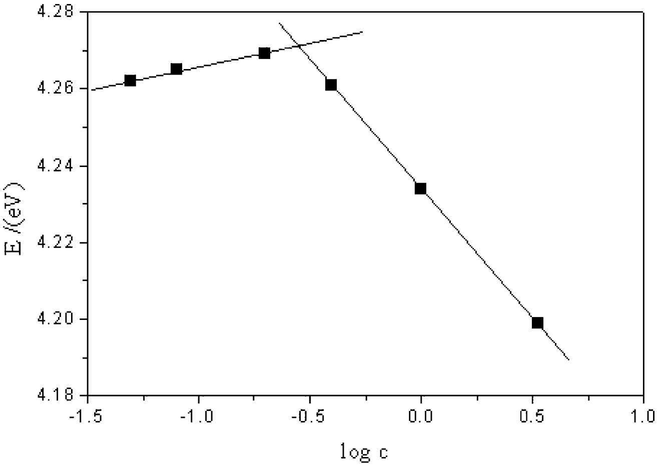

Fig. 2 Variation of the absorbed energy in the UV as a function of the concentration of one fraction of PS ($M_w = 20{,}000$) in cyclohexane ($c^{**} = 0.22$ g/100 ml)

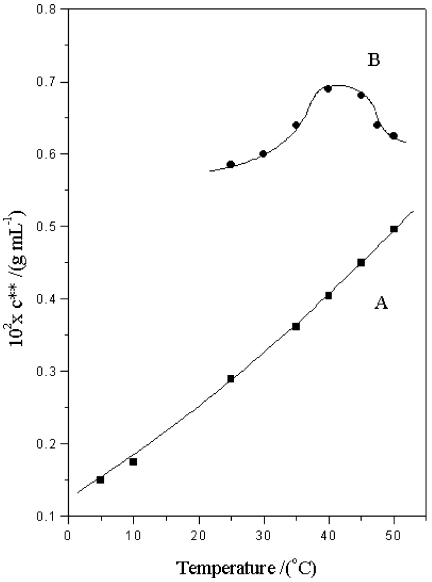

Fig. 3 Variation of the critical concentration c^{**}, determined by viscometry, as a function of the temperature for the PS homopolymer, $M_w = 52000$, (*curve A*) and the PS–poly(methyl methacrylate) (PMMA) diblock copolymer, $M_w = 50000$, (*curve B*) in chloroform

segregated conformation (core and shell model) [13, 14], although below the transition the copolymer presents a segregated conformation (dumbbell model) and above the transition temperature a pseudo-Gaussian conformation is adopted [13]. The decrease of the molecular volume of the PS–PMMA copolymer, at the transition temperature, is expressed now by an increase in c^{**}.

Experimental

The diblock copolymers PS–PMMA were synthesized anionically by us in the "Charles Sadron" Institute in Strasbourg in the laboratory of P. Rempp, to whom we are very grateful. Their polydispersity, as checked by gel permeation chromatography, was always lower than 1.15. Their composition was PS/PMMA 1/1 (checked by differential refractive index analysis and also by NMR).

The viscosity measurements were conducted using a Schott Geräte automated viscometry unit equipped with Ubbelohde-type viscometers for in situ dilution. The temperature was controlled to within ±0.05 °C using a thermostable water bath.

The UV spectra were recorded with a UV-V15 Carl Zeiss Jena spectrophotometer in 2-cm cells.

Results and discussion

c^{**}, as shown in previous works [1, 2, 3, 4, 6], is determined by the change in the slope of the Huggins presentation of viscosity results (Fig. 1) and by the change in the slope in the representation of the variation of the absorbed energy as a function of the polymer concentration in UV measurements (Fig. 2) [5]. c^{**} is not the same in Figs. 1, 2 although the PS fraction is the same. This is due to the fact that in the static state (UV measurements) we have an enhancement of the number of entanglements per chain [7] which leads to the appearance of c^{**} at lower concentration than in the dynamic state (viscosity measurements).

Viscosity measurements

We have shown that the variation of c^{**} of a homopolymer with temperature increases smoothly with increasing temperature. Nevertheless in Fig. 3(curve A) we present again the variation of c^{**} of PS of molecular mass 52,000, in chloroform. In Fig. 3(curve B) we

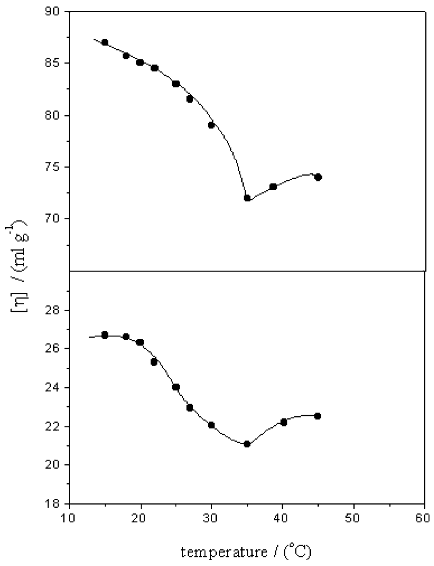

Fig. 4 Variation of the intrinsic viscosity as a function of temperature for two fractions of PS-PMMA in chloroform

present the variation of c^{**} with temperature of a PS–PMMA diblock copolymer of molecular mass 50,000, in the same solvent.

As we can see in Fig. 3, curve B, c^{**} presents a maximum value in the region of 40 °C and this behavior is different from the behavior of the PS homopolymer (Fig. 3, curve A).

Accepting that c^{**} increases when the hydrodynamic volume of the polymer coils decreases, in the region of 40 °C the block copolymer must present a decrease in its hydrodynamic volume. Indeed, presenting the variation of intrinsic viscosity, $[\eta]$, as a function of the temperature for two fractions of the PS–PMMA copolymer in $CHCl_3$ (Fig. 4) we can see this decrease of $[\eta]$. In this region of 40 °C we must indicate that the intrinsic viscosity of the homopolymers does not present any discontinuity.

UV measurements

With the use of the UV technique we obtained c^{**} with high accuracy (Fig. 2). The variation of c^{**} of a PS homopolymer with temperature (Fig. 5, curve A) presents a smooth increase as in the case of viscosity measurements (Fig. 3, curve A). On contrast, the variation of c^{**} with temperature of the same fraction of the PS–PMMA copolymers of Fig. 3, curve B (viscosity measurements), presents a maximum in the same temperature region (40 °C) as we can see in Fig. 5, curve B.

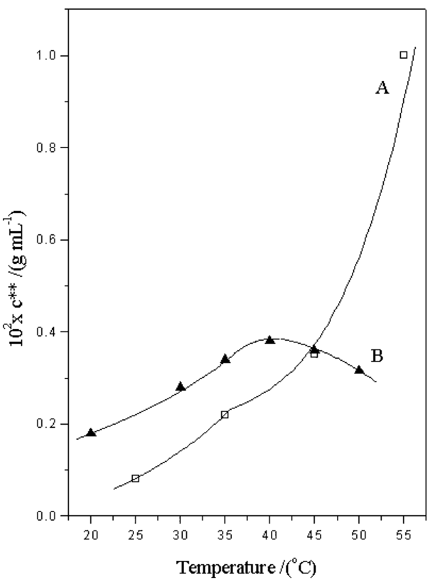

Fig. 5 Variation of c^{**}, determined by UV measurements, as a function of temperature for the PS homopolymer, $M_w = 20{,}000$, (*curve A*) and the PS–PMMA, $M_w = 50{,}000$, diblock copolymer (*curve B*), in cyclohexane

We must note here that, as we have already observed [5], c^{**}, of a given polymer sample, determined in the static state (UV) is lower than the critical concentration determined in the dynamic state (viscometry) and this is also observed for the same fraction of the copolymer (Figs. 5, curve B, 3, curve B).

It is worth noting that although the molecular mass of the PS homopolymer is the same as the molecular mass of the PS–PMMA block copolymer ($M_{wPS} = 52{,}000$, $M_{wPS\text{–}PMMA} = 50{,}000$) the c^{**} values of the copolymer (Fig. 3, curve B) are higher than the c^{**} values of the PS homopolymer (Fig. 3, curve A). This is attributed to the compression of the chain of the copolymer owing to the incompatibility between the internal and the external blocks of a "core–shell" type conformation, which is predominant especially in the region of the conformational transition [14]. In other words, the hydrodynamic volume of the copolymer is lower than the hydrodynamic volume of the corresponding homopolymer and consequently we observe a higher value of c^{**} for the copolymer.

In conclusion, the results presented in this work clearly indicate that c^{**} is sensitive to any change of the hydrodynamic volume of the macromolecular coils. This result allows the determination of c^{**} in order to study all the changes of polymer conformations which are related to their hydrodynamic volume. These results also confirm the existence of c^{**} beyond any doubt, which in the past had been treated with certain skepticism.

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