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Differentiation between conformational transitions of polymers and the transition observed near the theta conditions

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SUMMARY

The differentiation between the conformational transitions of polymers and the transition observed near the θ conditions has been investigated. The conformational transitions are related with side-group effects and vanish under the influence of an appropriate amount of a polar solvent. In the contrary, the transition observed in the vicinity of the θ temperature is related with chain-backbone effects. The addition of a polar solvent shifts this transition to a different temperature in accordance with the resulted change of the θ temperature of the system.

INTRODUCTION

The conformational transitions of synthetic polymers in dilute solution have been the subject of a great number of works during the last decades (1-15). These transitions deal with abrupt changes of the dimensions of the macromoleculare chains and appear in a given temperature. The phenomenon has been attributed to a different mobility of the side-groups of the chain, below and above the transition temperature.

Recently, a new type of polymer transition has been observed dealing with dimensions of the chain in the vicinity of the θ conditions (16-19). This transition is induced by changing the temperature of the solution when the polymer is dissolved in a single (16) or in a binary (of constant composition) (19) θ solvent, as well as by changing the solvent composition at constant temperature when the polymer is dissolved in a binary solvent mixture (18).

Both transition phenomena affect mainly the short range interactions as demonstrated by sudden changes of the K_θ parameter which expresses the flexibility of the chain.

The aim of this article is to investigate the differences between these two transition phenomena.

EXPERIMENTAL PART

The samples of poly(2-vinylpiridine) PV_2P ($\bar{M}_w$=58.000) and atactic poly(methyl methacrylates) PMMA ($\bar{M}_w$=93.000) were prepared by anionic polymerization and present very low polydispersity.

All reagent were analytical grade chemicals from Merck and were used as received. The solvent mixtures were prepared by volume using a Schott- Gerate automatic injection system with a precision of ± 0.01%.

Viscosity measurements were carried out in a Schott-Gerate AVS automated viscosity measuring system equiped with an automatic injection system for in situ dilutions. The viscometers used were of the Ubbelohde type. The reproducibility of the efflux time was better than ± 0,05 s. The intrinsic viscosity $[\eta]$ was calculated by means of the Huggins relationship and was expressed in $ml.g^{-1}$. The initial concentration of the polymers in the solutions was lower than $0,8 \times 10^{-2}$ $g.ml^{-1}$.

RESULTS AND DISCUSSION

It is well known that PMMA and other polymethacrylates undergo conformational transitions in dilute solutions (6-14). More precisely the conformational transition of atactic PMMA appears in a few good solvents in the temperature range between 40° and 55°C (6). Recently we have reported that the same polymer presents a transition in acetonitrile, which is a Θ solvent for PMMA in 45°C, within the same temperature range. As it has been shown this transition is closely related to the Θ conditions of the polymer (17).

From the first sight, the two phenomena seem to be different, as one can see comparing the plots of the K_Θ parameter versus T (fig.1). The conformational transition is characterised by two dinstict flexibilities of the chain (the value of K_Θ remains lower above the transition point) while in the transition observed above the Θ point the flexibility of the chain is the same below and above the transition point.

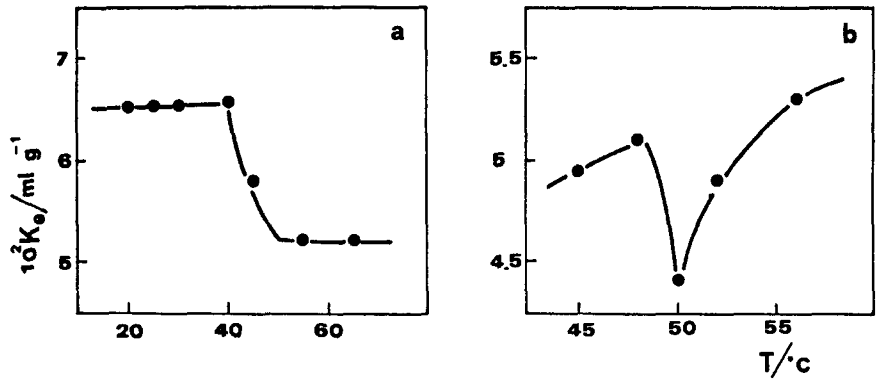

Fig.1. Temperature dependence of the unperturbed dimensions parameter K_θ for PMMA in (a) Benzene, ref.(6) (b) Acetonitrile,ref.(17).

Another feature, which has been shown, is that the conformational changes are induced mainly by side-groups effects and not by the rotation of the carbon atoms of the main chain (20). This implicates that the conformational transitions are related to the temperature and the nature of the solvent. Moreover the conformational transitions vanish when an appropriate amount of a polar solvent, giving certain interactions with the side-groups, is added to the polymer-solvent system (3).

In the contrary, the transition above θ temperature is a phenomenon accuring in any polymer and is observed in the θ region independent of the nature of the solvent and the temperature where the θ conditions occur. Consequently this transition must be attributed to a peculiar behaviour in the mobility of the chain backbone. Thus the addition of the polar solvent must not suppresses the phenomenon as it is observed for the conformational transitions.

In order to verify the above assumptions, both transition phenomena of PMMA were studied and in both cases the addition of a polar solvent was invastigated.

The temperature dependence of the intrinsic viscosity of PMMA in benzene is shown in fig.2a. The observed discontinuity shows the predictable conformational transition of PMMA as it has been reported by Katime et al(6). Figure 2b shows the viscosimetric behaviour of the PMMA-Benzene system after

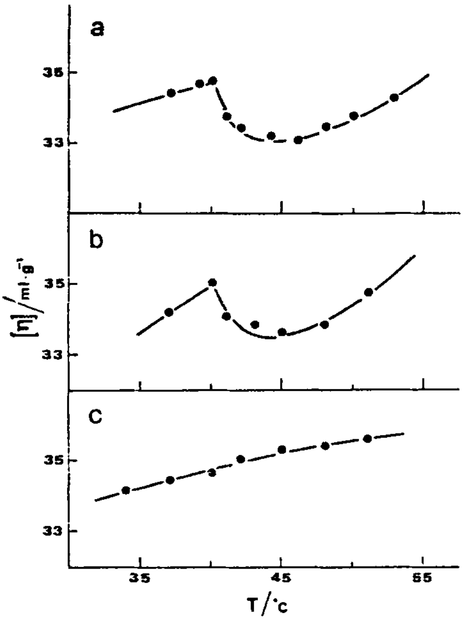

Fig.2.

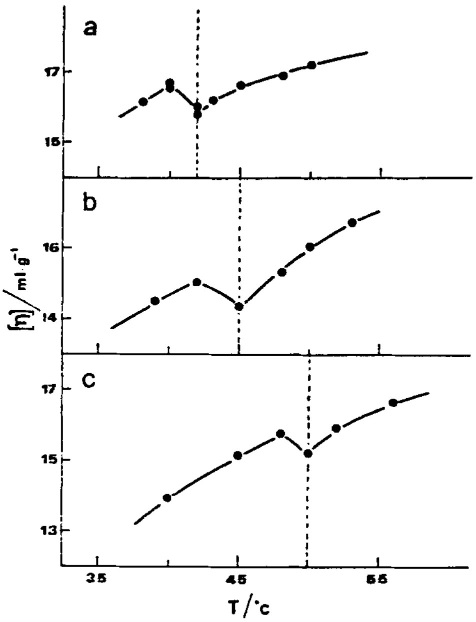

Fig.3.

Fig.2. Temperature dependence of the intrinsic viscosity [η] of PMMA in (a) Benzene, (b) Benzene (99%) + $CHCl_3$ (1%), (c) Benzene (98%) + DMF (2%).

Fig.3. Temperature dependence of the intrinsic viscosity [η] of PMMA in (a) Acetonitrile (98%) + DMF (2%), (b) Acetonitrile (99%) + $CHCl_3$ (1%), (c) Acetonitrile.

the addition of 1% $CHCl_3$. The transition appears in the same temperature showing that the polar solvent $CHCl_3$ does not present specific interactions with the polymer and the phenomenon remains visible. Further, a more drastic polar solvent was used. In figure 2c, it is clear that the transition of PMMA has been eliminated after the addition of 2% DMF to the system. This behaviour must be attributed to specific interactions between the side-groups of PMMA and the DMF molecules which inhibit the ordering of the side groups and consequently the transition vanishes.

An analogous study was performed with the system PMMA-acetonitrile where a transition closely related to the θ conditions has been observed. The addition of 1% $CHCl_3$ or even 2% DMF does not suppress the phenomenon, but the transition appears now in lower temperatures because we have a displacement of the θ conditions, after the addition of good solvents of PMMA (fig.3)

The above results corroborate the assuption that the transition near the θ point is not related to the ordering of the side-groups and concequently must be attributed to a sudden change in the mobility of the chain backbone.

As it has been reported by Dondos et al (3, 4) PV_2P undergoes a conformational transition in dilute solution appearing between 20° and 30°C in THF, as well as in benzene which is a θ solvent for PV_2P at 15°C. Moreover the transition vanishes when 1% $CHCl_3$ is added to the solution of PV_2P in benzene. If the transition above the θ conditions exists, the transition temperature must be shifted in lower temperatures after the addition of an amount of a good solvent of the polymer.

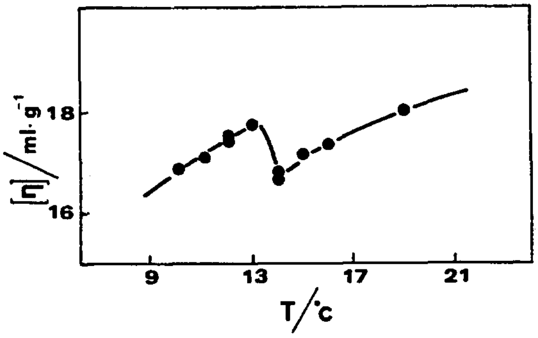

Fig.4. Temperature dependence of the intrinsic viscosity $[\eta]$ of PV_2P in Benzene (99%)+$CHCl_3$ (1%).

Viscosimetric measurements were obtained in the system PV_2P-Benzene + 1% $CHCl_3$ in lower temperatures than 17°C, a range which had not been investigated. Figure 4 shows the known behaviour of the transition observed above the θ conditions, which appears now at 13°C. In the contrary, the transition is not observed in the system PV_2P-THF + 1% $CHCl_3$ because THF is a good solvent of the polymer (21). Also the displacement of the transition temperature after the addition of 1% $CHCl_3$ is more pronounced, as it is predicted (18), because the system yields very high preferential adsorption of $CHCl_3$ on the polymer chain (3).

In conclusion, PV_2P also exhibits a transition phenomenon above its Θ conditions in benzene which, however, is obscured by a more pronounced conformational transition occuring in the same temperature range. The phenomenon is revealed in lower temperatures when an amount of a good solvent (i.e. $CHCl_3$) is added to the system.

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