

Effect of Temperature and Thermodynamic Quality of Solvent on Viscosity of Polystyrene

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Summary: The intrinsic viscosity $[\eta]$ of polystyrene is investigated with respect to temperature (15°-45°C) and thermodynamic quality of the solvent. These measurements are made using the pure as well as mixed solvents (solvent/non-solvent). From the observations, it is proved that one gets a maximum in the intrinsic viscosity, when it is plotted against temperature, secondly the $[\eta]$ decreases with the decrease in the thermodynamic quality of the solvent.

Introduction

The investigation of the dependence of viscosity $[\eta]$ of polymer on concentration C , temperature T , nature of solvent and molecular weight M is of great importance for the commercial production and processing of polymers [1,2]. On the other hand the literature shows different behaviour of polymer viscosity with respect to the above mentioned parameters. For example Kawai et al. [3] and other workers [4,5] in this field showed that the intrinsic viscosity of polymers when plotted against T , gives a maximum at a temperature denoted by T_m . While the observations of other scientists [6] is different. Similar discrepancies also exist for the effect of solvent on the viscosity of polymer solutions [2]. Keeping in view the above facts and the importance of polystyrene in daily life the present work was undertaken to investigate the effect of temperature and nature of solvent on the intrinsic viscosity of the polymer. It would thus help in verifying the Kawai phenomenon and to give the possible explanation for the same.

Experimental

Materials

Polystyrene, having molecular weight equal to 5.93×10^4 grams/mole is used for investigation. The solvents used were dioxane, benzene and cyclohexane, while the precipitants used were ethanol and butanol. All the solvents and precipitants were of analar grade and were obtained from E.Merck. Thus no further purification was carried out.

Procedure

The viscosity of the polymer was measured in pure solvent as well as in a mixture of solvents and precipitants using Ostwald viscometer. The measurements were made by varying the concentrations of polymers, solvent to precipitant ratio and temperature (15°-45°C) of the system. During the measurements, the temperature was controlled to $\pm 0.01^\circ\text{C}$ and efflux time reproducibility to $\pm 0.1\%$. Intrinsic viscosities $[\eta]$ were measured in the usual manner by extrapolating

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both η_{sp}/c and $\ln \eta_r/c$ to zero concentration.

Results and Discussion

The η_{sp}/c and $\ln \eta_r/c$ values were plotted against concentration for extrapolation purpose. The intrinsic viscosity so obtained was plotted against the vol.% ratio of butanol (precipitant) in benzene (solvent) and ethanol in dioxane individually (Fig. 1). The results show that the intrinsic viscosity is very much dependent

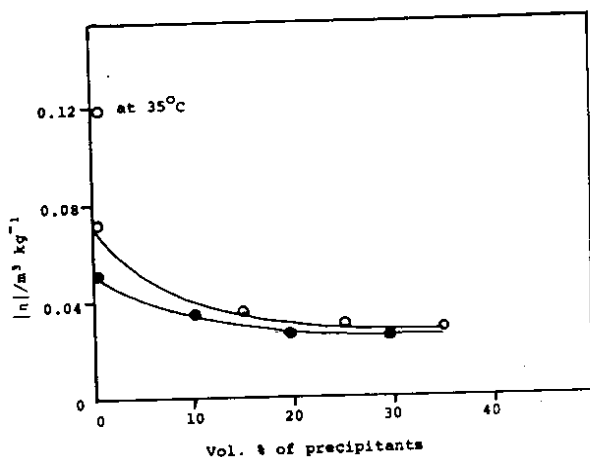


Fig.1. Dependence of $[\eta]$ on vol.% of (o) butanol in benzene and (.) ethanol in dioxane measured at 25°C.

on the thermodynamic quality of solvent and it decreases as the quality of the solvent deteriorates irrespective of the solvent used. This may be due to the fact that the degree of aggregation rises as the ratio of non-solvent increases and the rigidity in the chain of the polymer also increases [2]. The intrinsic viscosity is also calculated at different temperatures and is plotted against temperature as shown in figure 2. This

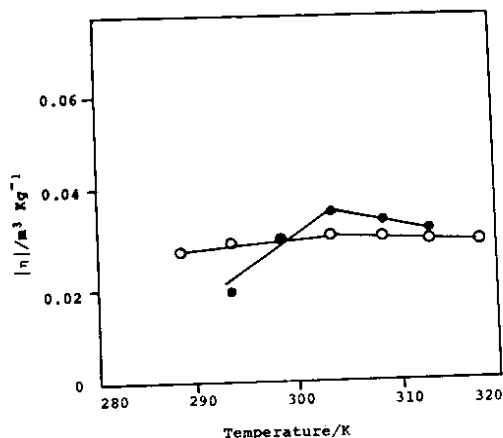


Fig.2. Dependence of intrinsic viscosity on temperature in (o) butanol/benzene (25:75) and in (o) cyclohexane.

figure shows that the intrinsic viscosity firstly increase, reaches to maximum and then decreases irrespective of the solvent used. The T_m was found to be 30°C for both the solvents. The $\ln [\eta]$ is also plotted against temperature and one gets also the maximum (Fig. 3).

This type of behaviour is also observed by other scientists [3-5]. With the varying temperature, there are different factors which control the viscosity of polymers solutions such as:

i) Change of quality of the solvent: This can lead to only higher intrinsic viscosity of the solution by increasing the temperature.

ii) Change in concentration of the solution: The increase in the temperature will reduce the concentration, due to the expansion in the solvent volume and vice-versa. The error so

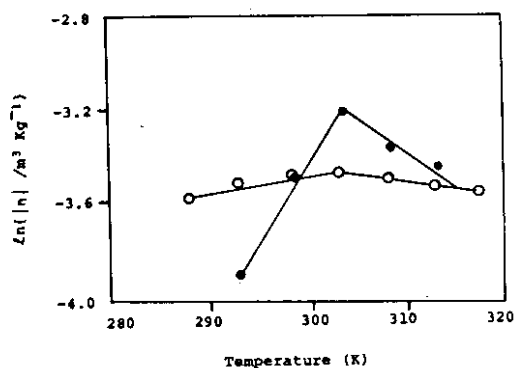


Fig. 3. Dependence of $\ln [\eta]$ on temperature, the symbols have the same meanings as in Fig.2.

introduced may provide a maximum in the intrinsic viscosity, but theoretically this maximum should not be so pronounced as has been observed in the present work and also reported by others [3-5].

iii) The expansion in the viscometer bulk and capillary with the rise in temperature and vice-versa may introduce an error.

iv) One of the important factor which controls the phenomenon is critical solution temperature. When a system has an upper critical solution temperature (UCST), the quality of the solvent improves as temperature rises, the solvent itself becoming better and leads to effectively breaking down the structure for better characteristic at high temperature. When, however, a system has a lower critical solution temperature (LCST), the solvent deteriorates as temperature rises and breaks structure up less well at high temperature [7]. The fall in viscosity with rise of temperature in the first case is less than in the second.

The type of critical solution temperature also affects the temperature

coefficient of the intrinsic viscosity [8,9]. In systems with UCST the molecular coil swells more as temperature rises, leading to an increase in $[\eta]$, while in systems with LCST it swells less, which lowers solvent quality. The value of $[\eta]$, therefore, falls with rise of temperature. The above discussion leads to the conclusion that the intrinsic viscosity will provide a maximum when plotted against temperature irrespective of the polymer and solvent used for investigation. On the other hand some of the scientists [2,6] did not observe such maximum in the $[\eta]$. The data obtained by Tager [2] shows that it decreases with the increase in temperature while Hadijchristidis et al. [6] has shown that it increases while the increase in temperature. The difference in observations may be due to not covering whole range of temperature required for such phenomenon.

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