cerned, this method reproduces experimental values of both $\langle S_i^2 \rangle$ and χ_{0i} with high precision (see Table I) and should be of practical value. For a reasonably symmetrical system with a small $\chi_{12}°$, eq 30 with eq 23 and 31 may be used instead of eq 26 with eq 22 and 23.

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Registry No. PS, 9003-53-6; PMMA, 9011-14-7.

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$$\chi_{0i} = g_{0i} - (\partial g_{0i}/\partial \phi)_{\phi=0} \quad (i = 1 \text{ or } 2)$$

$$\chi_{12} = g_{12}$$

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(19) Since eq 30 has been claimed to be incorrect by some people,[20] we add some words to justify it. In the mentioned symmetrical case with a small $\chi_{12}°$, eq 26 reads

$$\chi_{12} = (1 - 2\chi_{0i}°)(1 + \kappa)h_0(\bar{Z}_{12}) - (1 - 2\chi_{0i}°)h_0(\bar{Z}) \quad \text{(R1)}$$

with $h_0(\bar{Z}_{12}) = h_0(\bar{Z} + \kappa\bar{Z})$ being expanded around $\chi_{12}° = 0$ or $\kappa\bar{Z} = 0$ as

$$h_0(\bar{Z}_{12}) = h_0(\bar{Z}) + \kappa\bar{Z}[\mathrm{d}h_0(\bar{Z})/\mathrm{d}\bar{Z}] + \ldots \quad \text{(R2)}$$

Inserting eq R2 in eq R1 and neglecting higher terms in κ, we have

$$\chi_{12} = \kappa(1 - 2\chi_{0i}°)[h_0 + \bar{Z}(\mathrm{d}h_0/\mathrm{d}\bar{Z})] = \chi_{12}°[\mathrm{d}(\bar{Z}h_0)/\mathrm{d}\bar{Z}] \quad \text{(R3)}$$

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Investigation of Transition Phenomena of Polymers in Dilute Solutions by Gel Permeation Chromatography

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ABSTRACT: Gel permeation chromatography (GPC) has been used as a new technique for the study of temperature-induced polymer transitions in dilute solutions. Using a GPC apparatus with controlled temperature, we have studied the transition of polystyrene in solution in the binary solvent mixture benzene–methanol (74:26 v/v) and the transition of the triblock copolymer poly(methyl methacrylate)–polystyrene–poly(methyl methacrylate) in solution in tetrahydrofuran. The GPC method has corroborated our previous findings on transition phenomena of polymers observed near Θ conditions.

Introduction

In recent years many papers have appeared dealing with the transition phenomena of macromolecular chains in dilute solutions. Some of these are reported as helix–coil transitions, mainly found for biopolymers and wormlike polymers.[1-5] Another type of transition is reported as conformational[6-28] and is related to an order–disorder transition of the side groups of the macromolecular chains. In the case of block and graft copolymers the transtion phenomena are related to the segregated and nonsegregated conformations of these copolymers.[29-40]

Recently, we observed a new type of transition closely related to Θ conditions.[41-43] More precisely, this transition appeared just above the Θ conditions and was observed either by changing the temperature of the solution when the polymer is dissolved in a single solvent or by chainging the solvent composition at constant temperature when the polymer is dissolved in a binary solvent mixture. This transition seems to be related to an abrupt augmentation of the mobility of the chain backbone affecting mainly the short-range interactions. The phenomenon has also been observed by Nishio et al.;[44] using photon correlation spectroscopy they found strong fluctuation in the chain density in the same temperature range.

All the above transition phenomena have been studied by a variety of experimental techniques. Some of these techniques, e.g., IR spectroscopy,[5,7,39] UV spectroscopy,[6,40] ultrasonic relaxation,[21] and quasi-elastic neutron scattering,[28] are concerned with local changes in the macromolecular chain. There are other techniques, e.g., static light scattering,[1,2,7,9,10,34] refractometry,[13,16,18,19,25] and viscometry,[14-20,22-26,29-32,41-43] that deal with the overall dimensions of the macromolecular chains.

Gel permeation chromatography has been established as a very useful technique for studying macromolecules. One of the principal aims of the GPC method is to de-

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termine average molecular weights and molecular weight distributions of polymers. Some other applications of GPC are the investigation of the composition[45] and architecture[46] of copolymers, the degree of branching of a polymer,[45] and its preferential adsorption when it is dissolved in a solvent mixture.[47]

The separation mechanism of the GPC technique is based on the effective size of the macromolecules in solution or, more precisely, on the hydrodynamic volume of the macromolecules, as established by Benoit et al.[48,49]

In the present article we propose a new GPC application for the investigation of temperature-induced polymer transitions, based on the variation of the hydrodynamic volume of the macromolecular chains that usually accompanies such transitions. More precisely, the GPC technique is used to study the new type of polymer transition observed near the Θ point[41,43] and the conformational transition of a block copolymer.[30]

Theoretical Background

The separation of macromolecules by GPC is considered on the basis of equilibrium thermodynamics. The separation mechanism of macromolecules within a porous packing during a chromatographic process is determined by the change in free energy of the macromolecule, ΔF, occurring when it passes from the channels of the mobile phase of the column into a pore of the sorbent, i.e., the stationary phase. The retention volume V_R of a macromolecule in a porous packing is given by

$$V_R = V_o + K_{GPC} V_i \qquad (1)$$

where V_o is the total volume of the mobile phase, V_i is the total volume of the stationary phase, and K_{GPC} is the distribution coefficient, which can be expressed in terms of the free energy change[50,51] by

$$K_{GPC} = \exp(-\Delta F/kT) \qquad (2)$$

where k is Boltzmann's constant.

Assuming now that secondary effects are involved during the chromatographic process, the separation mechanism is expressed best by the Dawkins formula[52-54]

$$V_R = V_o + K_D K_P V_i \qquad (3)$$

where

$$K_D = \exp(\Delta S/K) \qquad (4)$$

which is the distribution coefficient for the steric exclusion mechanism (SEM) and is combined with the loss of conformational entropy during interface transition, i.e., the primary separation mechanism, and

$$K_P = \exp(-\Delta H/kT) \qquad (5)$$

which is the distribution coefficient for solute–sorbent interactions involving adsorption and partition effects, i.e., the secondary separation mechanism.

In order to study temperature-induced conformation transitions by GPC we must determine the distribution coefficient for the steric exclusion mechanism, which is correlated with the overall dimensions of the macromolecule by equations of the type

$$K_D = f[(\bar{R}^2)^{1/2}/r] \qquad (6)$$

where $(\bar{R}^2)^{1/2}$ is the mean-square radius of gyration of the macromolecule and r is the radius of the sorbent pore.[51] According to eq 6, any variation of the size of the macromolecule will be reflected in the K_D parameter. More precisely, the analytical form of eq 6 indicates that the greater the dimensions of the molecule, the smaller the distribution coefficient for the steric exclusion mechanism.

Experimental Section

The atactic polystyrene samples were prepared by anionic polymerization and have very low polydispersity ($\bar{M}_w/\bar{M}_n < 1.1$). The triblock methyl methacrylate–styrene–methyl methacrylate (PMMA–PS–PMMA) copolymer containing 53% styrene was prepared anionically by standard experimental techniques. The molecular weight of the copolymer measured by light scattering in tetrahydrofuran is $\bar{M}_w = 4.25 \times 10^5$ and the polydispersity $\bar{M}_w/\bar{M}_n \simeq 1.3$. All samples were supplied by the Centre des Recherches sur les Macromolécules in Strasbourg (France).

Benzene (BZ), methanol (MeOH), and tetrahydrofuran (THF) were analytical or HPLC grade (Merck; putity 99.7%). All solvents were filtered before use by vacuum filtration using 0.5-μm filters according to standard methods. The solvent mixture was prepared by volume using a Schott–Gerate automatic injection system with a precision of ±0.01%.

The GPC measurements were performed with a Waters Associates Model 201 instrument equipped with a Model 401 differential refractometer as detector. Two different series of columns were employed during the chromatographic experiments. For the PS analysis three Waters Associates μBondagel E-125, E-500, and E-1000 columns in series were used with actual pore sizes 125, 500, and 1000 Å, respectively. For the PMMA–PS–PMMA copolymer analysis three Waters Associates μStyragel columns in series were used with nominal pore sizes 10^3, 10^4, and 10^5 Å, respectively. The columns were temperature controlled via a Waters temperature control system consisting of a temperature control module and a column heater. This system provides a stable operating temperature to within ±0.1 °C. The flow rate of the mobile phase was 1 mL·min^{-1}. The concentrations of the PS and the copolymer solutions were 6×10^{-4} and 1×10^{-3} g·mL^{-1}, respectively. The injection volumes were always 100 μL. Each measurement was performed four or five times, and the retention volume V_R is the mean value. The standard error never exceeded 1%.

Viscosity measurements were carried out in a Schott–Gerate AVS automated viscosity measuring system equipped with an automatic injection system for in situ dilutions. Viscometers were of the Ubbelohde type and were specially designed for use in conjunction with the AVS system. The temperature was controlled with a Haake E-3 immersion circulator to within ±0.02 °C. The efflux times for solvent and solutions ranged between 100 and 200 s, and the reproducibility was better than 0.02 s. The limiting viscosity numbers $[\eta]$ were calculated by means of the Huggins relationship and are expressed in mL·g^{-1}. The initial concentration of the polymers in solution was less than 0.45×10^{-2} g·mL^{-1}, assuring that we are in dilute solution.

Results and Discussion

The study of transition phenomena by GPC in the vicinity of Θ conditions as a function of temperature involves some difficulties concerning the nature of porous media of the columns and the solute–sorbent interactions. The first problem deals with the swelling sorbents when the eluent causes a contraction of the gels of the packing, thereby increasing undesirably the interstitial volume. The second problem concerns the abnormal retentions that have been observed when polymers are eluted in poor or Θ solvents with any type of packing.[52,54-57]

Using cyclohexane as solvent with a rigid sorbent (μBondagel) in order to detect the transition of PS already determined by viscometry, we observed strong adsorption effects giving a K_{GPC} value near unity; for this reason, the process produces uncertain results. In order to avoid the above difficulties, we used the binary solvent mixture benzene–methanol (74:26 v/v), having a solvent strength parameter[58] $\epsilon^0 \simeq 0.87$. The presence of the polar solvent suppresses the adsorption effects.[54]

Viscosimetric measurements were carried out with the PS sample in solution in the above solvent mixture, changing the temperature in the range 23–36 °C. In Figure 1a we give the variation of intrinsic viscosity $[\eta]$ as a

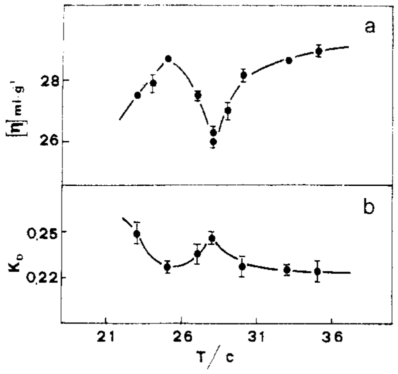

Figure 1. Variation of the intrinsic viscosity $[\eta]$ (a) and distribution coefficient for SEM K_D (b) as a function of temperature for the system PS($\bar{M}_w = 1.15 \times 10^5$)/BZ (74%) + MeOH (26%) (error bars represent the standard deviation).

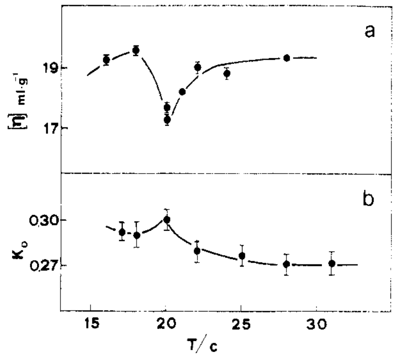

Figure 2. As in Figure 1 for PS($\bar{M}_w = 5 \times 10^4$).

function of temperature. It may be seen that there is a sharp discontinuity. This phenomenon appears above the Θ temperature, in agreement with our previous results,[43] as the expansion factor α_η^3 at the transition point approaches the value 1.08.

In the same temperature region we have performed chromatographic experiments using the same solvent mixture as eluent and silica gel modified by other groups (μBondagel) as porous packing. Measuring the retention volumes V_R of PS as a function of temperature and the interstitial and the porous volumes V_0 and V_i, which do not change with T, and taking K_P equal to unity since no adsorption effects take place, we have determined the distribution coefficients for the steric exclusion mechanism K_D by eq 3. In Figure 1b we display the variation of K_D as a function of T. As shown, the distribution coefficient exhibits a maximum in the same temperature range where the intrinsic viscosity presents a mimimum. This result shows that at 28 °C the macromolecular coil attains a minimum in its hydrodynamic dimensions (minimum in $[\eta]$), and therefore the K_D exhibits its maximum value.

In order to corroborate the above results, experiments were carried out under the same experimental conditions (sorbent and eluent) using now a PS sample of different molecular weight ($\bar{M}_w = 5 \times 10^4$). As expected, the transition point was shifted to a lower temperature, which is attributed to increased preferential adsorption[43] since the molecular weight of PS has been decreased. The viscosimetric results show that the minimum in the intrinsic viscosity $[\eta]$ vs. T appears now at 20 °C (Figure 2a). The expansion factor α_η^3 at the transition point takes the value 1.1, indicating that the phenomenon is observed above the intramolecular Θ conditions.

In addition, chromatographic measurements were performed and the retention volume was obtained as a function of temperature. In Figure 2b we present the distribution coefficient K_D as a function of T. The observed maximum in K_D vs. T appears at 20 °C, in excellent accord with the viscosimetric results and assuring that a transition in the dimensions of PS takes place.

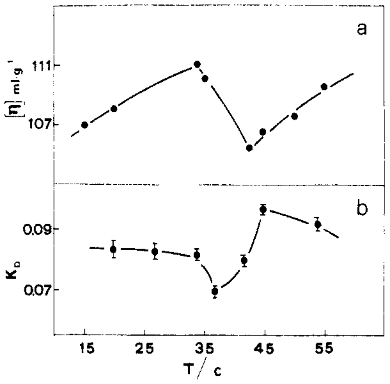

Figure 3. Variation of the intrinsic viscosity $[\eta]$ (a) and distribution coefficient for SEM K_D (b) as a function of temperature for the system PMMA-PS-PMMA/THF.

The change from a segregated to a "pseudo-Gaussian" conformation of the macromolecular chains of block copolymers involves an abrupt change in intrinsic viscosity in a given range of temperature. The variation of $[\eta]$ of the triblock copolymer PMMA-PS-PMMA in THF has already been published[30] and is reproduced in Figure 3a.

Chromatographic experiments were carried out with the same triblock PMMA-PS-PMMA copolymer using THF as eluent and cross-linked polystyrene gels (μStyragel) as a porous packing.

It is known that variation of temperature influences the interstitial volume V_0 and the porous volume V_i in swelling sorbents. Indeed, linear dependences of V_0 and V_i with T have been observed. Taking into account dV_0/dT, dV_i/dT, and $K_P = 1$ (no adsorption), we have calculated K_D as a function of T. The distribution coefficient K_D of this copolymer vs. T exhibits a discontinuity, showing that an abrupt variation in the conformation of the copolymer occurs between 37 and 45 °C, in accordance with viscosimetric and light scattering results.[34] Nevertheless, we observed a small difference in the temperature at which the maximum of K_D and the minimum of $[\eta]$ are obtained. This must be attributed to the different quality of the solvent used in the viscosimetric and chromatographic experiments, since the transition temperature in the case of copolymers depends on the quality of the solvent.[30]

Conclusion

We have shown that gel permeation chromatography can be used in the study of temperature-induced transition phenomena of macromolecules. The method exhibits very good reproducibility of the experimental results. It is very rapid compared with other techniques and requires only a very small amount of sample. The method may also prove useful in the study of biological macromolecules.

The viscosimetric and chromatographic results obtained in the present work also provide additional arguments concerning the existence of a transition in polymers closely related to the Θ temperature.

Registry No. PS, 9003-53-6; (PMMA)(PS) (block copolymer), 25034-86-0.

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Approximate Methods for Calculating Rotational Diffusion Constants of Rigid Macromolecules

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ABSTRACT: In this work we have derived a double-sum formula for the rotational diffusion coefficients of rigid particles modeled as assemblies of N beads. We also consider an alternative approach in which the hydrodynamic interactions are orientationally preaveraged. The approximate methods are applied to rigid rods, rings, and compact structures, and the performance of these methods is characterized by the percent deviations of their results from those obtained by a more rigorous procedure. The results are presented in the form of reciprocals of the rotational relaxation times, which are directly observable. The orientational-preaverage approximation, which requires the inversion of an $N \times N$ matrix, yields quite discrepant results. On the other hand, the double-sum formula, in addition to being computationally much simpler, gives deviations of a few percent only for all the cases studied here. Laterally, we have studied the influence of a 0th-order contribution to the rotational coefficients that should be included to account for the discrete size of the frictional elements.

I. Introduction

The rigorous Kirkwood–Riseman calculation of hydrodynamic properties of rigid macromolecules, modeled as a set of N spherical elements, requires the inversion of a $3N \times 3N$ matrix or the solution of systems of $3N$ linear equations with $3N$ unknowns.[1-4] The corresponding step in the computational procedure is time- and memory-consuming for the high N's needed often to describe well the intricate shapes of biological macromolecules. A similar situation arises when the hydrodynamics of flexible or semiflexible polymer chains is studied by simulation in

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