Some studies on the conformational transition of poly(phenyl methacrylate) in solution

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A sample of poly(phenyl methacrylate) synthesized via free-radical polymerization was studied in solution, as a function of temperature, using density, refractive index, dipole moment and viscosity measurements. All these measurements exhibit some anomalies in plots against temperature in the region 293–313 K (according to the method). All these studies suggest a conformational transition of the polymer macromolecule in solution due to specific interactions between phenyl rings in the side groups of the chain.

(Keywords: poly(phenyl methacrylate); conformation transition; dipole moment; viscosity studies; specific interactions)

INTRODUCTION

Reiss and Benoit[1] in 1961 published some observations on a conformational transition of polystyrene in solution connected with a peculiar variation of the average radius of gyration with rising temperature. Moraglio *et al.*[2] have confirmed these by observations of critical transition phenomena for isotactic and atactic polystyrene both in solution and in bulk in the same region of temperature. Since Reiss and Benoit published their suggestions various authors have confirmed the existence of a kind of thermally initiated transition and shown the molecular character of this transition[3,4].

The number of polymers that undergo a conformational transition caused by thermally initiated intramolecular interactions is continually increasing[5-7]. Our studies of fluorescence of poly(phenyl methacrylate)[8] showed possibilities of conformation transition of the polymer chain in solution in tetrahydrofuran (THF) in the region 290–300 K due to specific interaction between phenyl rings.

Katime *et al*[9] have reported a peculiar variation of the intrinsic viscosity of several fractions of poly(phenyl methacrylate) (PPhMA) with temperature in methyl isobutyl ketone. This peculiarity appeared with a maximum followed by a minimum depending on the fraction of polymer at about 298–308 K. They have explained the anomalous behaviour in terms of a conformational transition initiated by solvent. The phenomena observed in PPhMA might be considered as a conformational transition occurring in the polymer on a molecular scale. Possibly the specific interactions of phenyl rings characteristic of the fluorescence behaviour[8] appeared as a consequence of the flexibility of the main chain initiated by temperature. The aim of this work was to characterize the conformational transition of PPhMA in tetrahydrofuran. To obtain more information about the nature of the conformational transition and about the structure of the macromolecule of PPhMA in this transition region, we expanded the studies using different experimental methods.

This paper describes some studies of solution properties like viscosity, density, dipole moment of polymer macromolecule and refractive index as a function of temperature in the region of the conformational transition. To our knowledge, there are no completed studies, in the literature, on solution properties of PPhMA as functions of temperature.

EXPERIMENTAL

Poly(phenyl methacrylate) was prepared by free-radical polymerization at 343 K in solution in methyl ethyl ketone with nitrogen flow using azobisisobutyronitrile (AIBN) of concentration 10^{-2} mol l^{-1} as thermal initiator. The polymer was purified by multiple precipitation from acetone. The monomer, phenyl methacrylate, was prepared by reaction of methacryloyl chloride with phenol. The solvents, tetrahydrofuran (THF) and *p*-dioxane, were purified by standard procedures[10]. Butyl acetate of high purity was used. Viscosities were measured with an Ubbelhode viscometer. Molecular weights of PPhMA were calculated in agreement with equation (1) obtained by Tsvetkov *et al.*[11]:

$$[\eta] = 1.47 \times 10^{-4} M^{0.63} \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity in butyl acetate at 24°C. The molecular weight of PPhMA obtained from the above equation with intrinsic viscosity $[\eta] = 0.457$ (100 ml g^{-1}) is $M_v = 350\,000$.

Dielectric constants of solutions of PPhMA in dioxane of concentration 0–2×10^{-2} g ml^{-1} were measured with a

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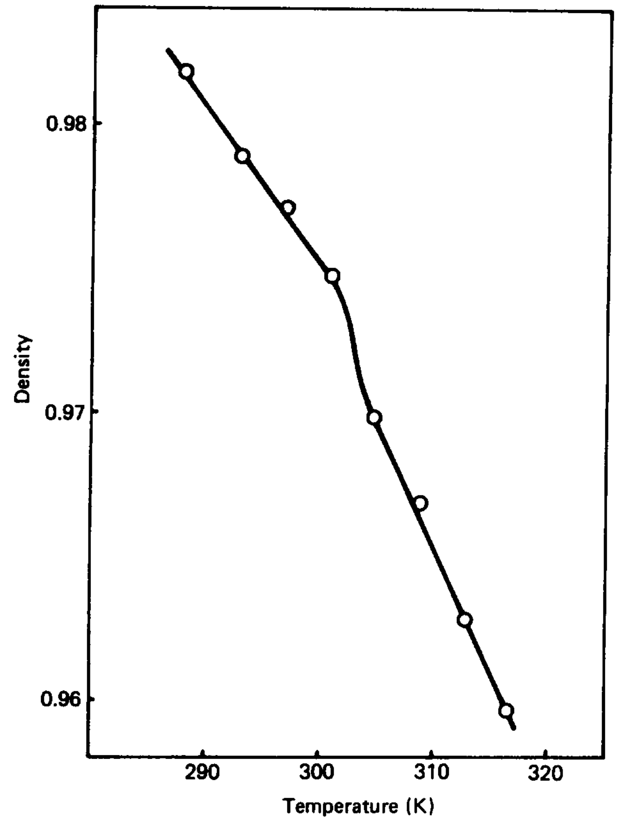

Figure 1 Dependence of density of PPhMA solution in THF on temperature

bridge at a fixed frequency of 1.0 MHz using a cylindrical, silver-plated thermostated cell of capacity 75 pF. The instrument was calibrated at each temperature of measurement using purified solvent and established values of its dielectric constants. The same concentrations of solutions were used for dielectric, density and refractometric measurements. Density was measured with a pycnometer with an accuracy of 10^{-4}; refractive index was measured using a Zeiss refractometer with an accuracy of 10^{-5}. Mean-square dipole moments $\overline{\mu^2}$ were calculated using the method of Fujita[12], which results in the following equation:

$$\overline{\mu^2}=1.646\times10^{-4}T\frac{M_2}{d_1}\frac{\varepsilon_1-1}{\varepsilon_1+2}\times\left(1+\frac{3\alpha}{(\varepsilon_1-1)(\varepsilon_1+2)}-\frac{\beta}{d_1}\right) \qquad (2)$$

where T is the absolute temperature, d_1 the density of the solvent, M_2 the molecular weight of the polymer, ε_1 the dielectric constant of the solvent,

$$\alpha=\lim_{w_2\to 0}(\mathrm{d}\varepsilon/\mathrm{d}w_2)$$

ε the dielectric constant of the solution and w_2 the weight fraction of the polymer,

$$\beta=\lim_{w_2\to 0}\mathrm{d}d/\mathrm{d}w_2$$

where d is the density of the solution of polymer. The values of α and β were obtained from the slopes of plots of ε and d respectively as a function of w_2, in the limit $w_2 \to 0$. Dipole moments thus calculated are expressed in debyes.

All the measurements were carried out at constant temperature with accuracy ±0.05°C.

RESULTS AND DISCUSSION

Preliminary studies of the fluorescence of PPhMA in THF and the observed peculiar variation with temperature[8] suggested the existence of a conformational transition in the region of 289–308 K. These studies and some preliminary measurements of PPhMA in THF with temperature[8] aroused our interest in the conformational transition and its nature.

According to our hypothesis that the observed transition is initiated mostly by temperature, it has been investigated first by methods used for second-order transition studies, i.e. density and refractive index measurements.

Density and refractive index studies

Our studies of the density variation of poly(phenyl methacrylate) solution in THF and in dioxane with temperature are shown in *Figures 1* and *2* respectively. A significant jump in density of PPhMA solution in THF was observed at a temperature of about 300 K in *Figure 1*. The effect of the jump in the density variation with temperature of dioxane solution is much less observable but is in the same region of temperature. The observed jump is similar to that predicted in specific volume variation with temperature by the statistical theory of macromolecules[13] for a second-order transition. The nature of the jump, in analogy to the statistical theory of macromolecules, would be connected with the transfer of the macromolecule from an expanded statistical coil to a compact system. This kind of compact structure with high probability of associated phenyl rings on adjacent units was predicted by studies of fluorescence[8]. To confirm results of our studies of density, the refractive index of

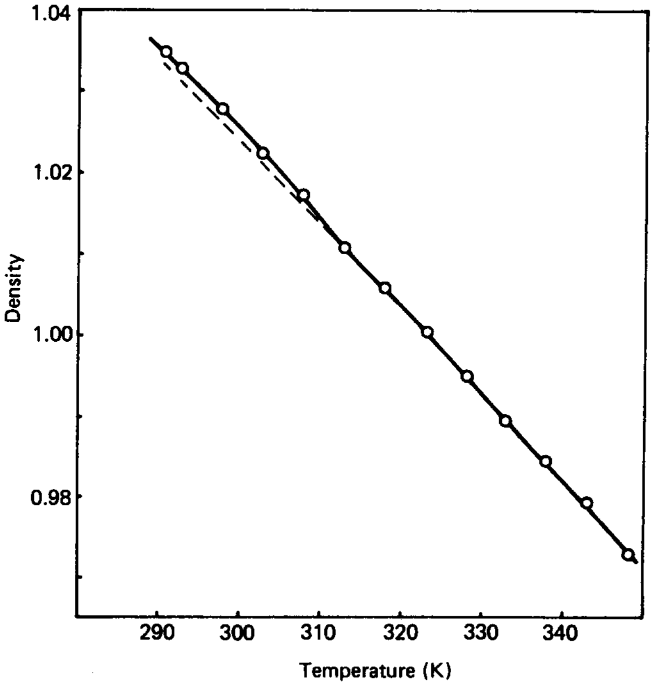

Figure 2 Dependence of density of PPhMA solution in *p*-dioxane on temperature

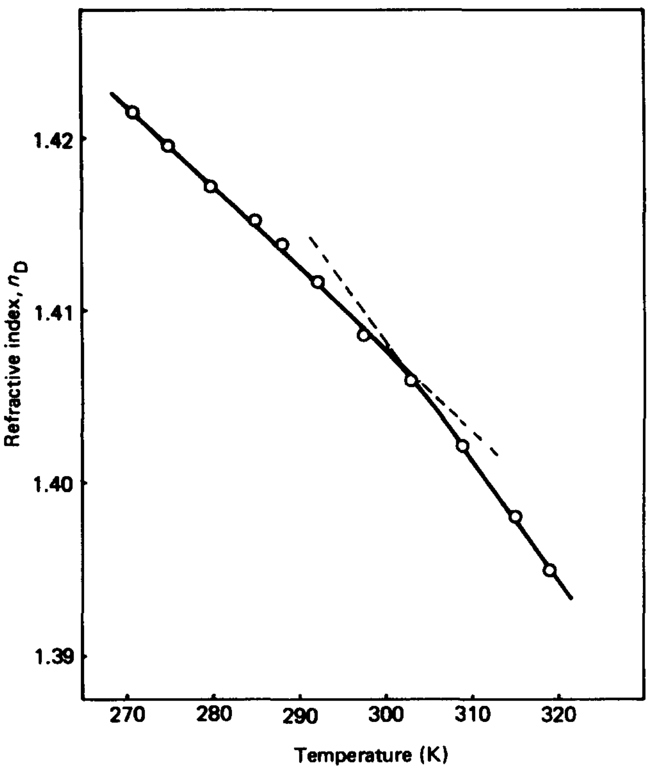

Figure 3 Dependence of refractive index of PPhMA solution in THF on temperature

PPhMA solution in THF as a function of temperature was investigated. Results of these studies are shown in *Figure 3*. As is characteristic for a second-order phase transition, a nonlinearity is observed. The change of slope in the dependence of the refractive index on temperature occurs at 303 K which is near the temperature of the jump in density at 300 K.

Viscosity studies

Intrinsic viscosities of PPhMA in THF solution at various temperatures have been obtained by extrapolation of plots of η_{sp}/c vs. concentration to infinite dilution. All the plots were linear and the intercepts gave us the intrinsic viscosities$[\eta]$. Our results for the thermal variation of intrinsic viscosity of PPhMA in THF in the range 278–318 K are shown in *Figure 4*. We can observe a weak increase of intrinsic viscosity with increase of temperature up to 290 K and a strong decrease of its value with further increase of temperature. Similar anomalies of the same magnitude were observed by Katime *et al.*[9] for thermal variation of intrinsic viscosity of PPhMA in methyl isobutyl ketone for the fraction of highest molecular weight. One method of determining the dimension of macromolecules from the measurements is Flory's equation:

$$[\eta] = \Phi(\bar{h}^2)^{3/2}/M \qquad (3)$$

where M is the molecular weight, Φ is a constant (for a number of linear macromolecules equal 2.1×10^{21} with $[\eta]$ in 100 ml g^{-1}) and $(\bar{h}^2)^{1/2}$ is the root mean square end-to-end distance (in cm). Our results of viscosity studies of poly(phenyl methacrylate) solution in THF and studies of the dimension of macromolecules obtained with equation (3) are presented in *Table 1*. The thermal variation of dimension of PPhMA in THF, i.e. of root mean square end-to-end distance, behaves similarly to intrinsic viscosity as we can see in *Table 1* (column 4). To characterize the effect of intramolecular hindrances on the flexibility or restriction to free rotation of the chain,

$$\sigma = (\bar{h}^2)^{1/2}/(\bar{h}^2)^{1/2}_{\mathrm{fr}}$$

was calculated. The $(\bar{h}^2)^{1/2}_{\mathrm{fr}}$ is the mean square end-to-end distance for a polymer macromolecule with a fixed angle between the main bonds and with the assumption of free rotation about each of the bonds. To calculate this quantity, a relation of conformational statistical theory in the following form was used:

$$\bar{h}^2_{\mathrm{fr}} = Nl^2(1+\cos\alpha)/(1-\cos\alpha) \qquad (4)$$

For a hydrocarbon chain the bond length l is the length of the C–C bond (1.54 Å) and the valence angle is close to the tetrahedral angle, i.e. to 109° 28′; so the $\alpha = \pi - 109° 28'$ (ref. 14).

Our studies of the flexibility factor σ given in *Table 1* (column 5) are in good agreement with the value obtained

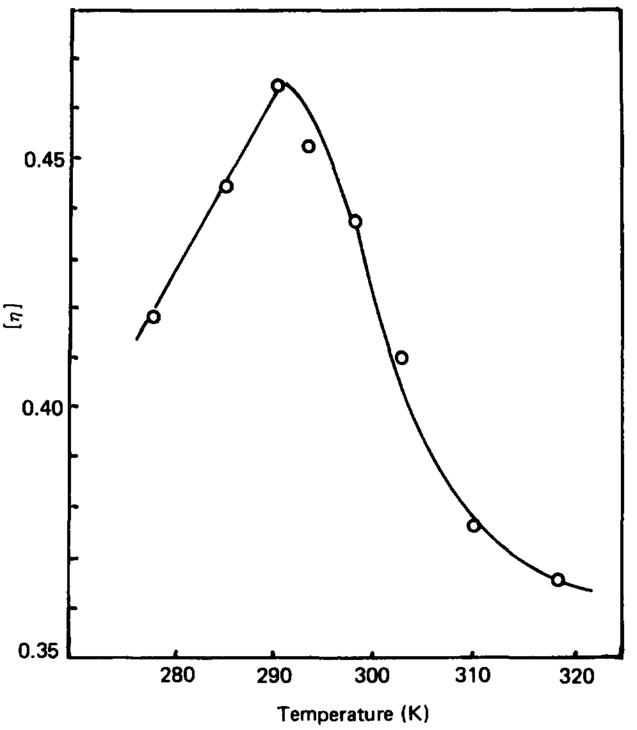

Figure 4 Dependence of intrinsic viscosity of PPhMA solution in THF on temperature

Table 1 Viscosity studies of poly(phenyl methacrylate) solution in tetrahydrofuran

Temp. (K)	$[\eta]$	K'	$(\bar{h}^2)^{1/2}$ (Å)	$(\bar{h}^2)^{1/2}/(\bar{h}^2_{\mathrm{fr}})^{1/2}$ [a]
278	0.416	0.35	411	2.83
285	0.445	0.37	420	2.90
290	0.465	0.38	426	2.93
293	0.453	0.53	422	2.91
298	0.438	0.65	418	2.88
303	0.410	0.82	408	2.81
310	0.375	0.92	396	2.79
318	0.366	0.96	394	2.71

[a] $(\bar{h}^2_{\mathrm{fr}}) = 145$ Å obtained in agreement with equation (4)

Table 2 Dipole moment studies of poly(phenyl methacrylate) and phenyl methacrylate in solution in *p*-dioxane

Temp. (K)	PPhMA $(\bar{\mu}^2/n)^{1/2}$	PhMA $(\bar{\mu}_0^2)^{1/2\,a}$	$\frac{(\bar{\mu}^2)^{1/2}}{(n\bar{\mu}_0^2)^{1/2}}$
289	2.91	2.66	1.09
293	2.76	2.67	1.03
298	2.43	2.54	0.96
303	2.02	2.51	0.80
308	2.01	2.52	0.78
313	1.45	2.40	0.60
323	1.15	2.37	0.50
328	0.84	2.36	0.35
338	0.75	2.19	0.34
343	0.60	2.07	0.29
353	0.50	1.99	0.26

[a] $(\bar{\mu}_0^2)^{1/2}$ = dipole moment of isolated monomer unit

by Tsvetkov *et al.*[11] for PPhMA in butyl acetate and with the value of 2.8 obtained by Hadjichristidis *et al.*[15]. The relatively high value of the flexibility factor represents the effect of steric hindrance on the flexibility of the polymer chain. After some increase (with temperature) of the flexibility factor at temperatures higher than 293 K, it decreases. The observed decrease of the flexibility factor at higher temperature is connected with a decrease in the dimension of the macromolecule caused by intramolecular interactions between side groups. It is possible that the interactions between the side groups cause the formation of a more compact and stiff phenyl complex.

To characterize intermolecular interactions between macromolecules of the polymer and between the polymer chain and the solvent, Huggin's equation[16] for a concentration-dependent specific viscosity (η_{sp}/c) was used:

$$\eta_{sp}/c = [\eta] + K'[\eta]^2 c \tag{5}$$

where K' is the coefficient of intermolecular interactions. Our results for Huggins's parameter K' of PPhMA in THF are given in *Table 1* (column 3). The increase of K' with temperature may be connected with the increase of intermolecular interactions between the macromolecules in some region of the transition.

All of the studies of the viscosity of PPhMA in THF suggest great variations in this solution behaviour in the temperature region of 298–303 K. This temperature region for the transition agrees with the transition observed by Katime *et al.*[9] from viscosity studies of a solution of PPhMA in methyl isobutyl ketone. Comparison of results of the viscosity studies of PPhMA in both solvents suggests a general conclusion that the most intensive parameter inducing conformational transition in PPhMA is temperature.

Dipole moment studies

Results of our studies of dielectric properties of poly(phenyl methacrylate) in solution in dioxane as a function of temperature are shown in *Table 2*. The dipole moments of PPhMA were calculated using equation (2). All the plots of dielectric constant and density variation with weight of polymer in solution (in the used region of concentration) were linear, giving α and β in equation (2) as the slopes of these dependences. As usual for the characterization of the dipole moment of a monomer unit in a polymer chain, the quantity $(\bar{\mu}^2/n)^{1/2}$, i.e. the average dipole moment of a monomer unit in a polymer chain (n is the number of units), was used. For some comparisons of the properties of the dipole moment in a polymer chain with that of an isolated molecule, similar studies for phenyl methacrylate (PhMA) in the same solvent were accomplished, and are included in Table 2. Our result for the dipole moment of PPhMA at room temperature (2.34 D) is bigger than that obtained by Burshtein *et al.*[17] (1.53 D). This difference is probably due to the different solvent used (benzene) and to a different structure of the macromolecule in solution, and seems to be real in comparison with the data for the temperature-dependent dipole moment. However, the theoretical calculation of the dipole moment of poly(vinyl chloride), which would be generally similar to PPhMA macromolecule, shown by Cantera *et al.*[18] predicts that the dipole moment should increase with increasing syndiotacticity. The sample of PPhMA used in these studies appeared mostly syndiotactic[19]. The dependence of the dipole moments of PPhMA and phenyl methacrylate on temperature is shown in *Figure 5*. As could be expected from the dimension studies, the dipole moment of PPhMA decreases with increase of temperature. Some decrease of the dipole moment of PhMA with increase of temperature may be due to the presence of oligomers. The dipole moment of PhMA (column 3) at a room temperature of 298 K (2.54 D) is acceptable in comparison with the dipole moment of a C=O bond, which is the dipole group in the polymer (2.48 D), cited after Hopfinger[20].

Marchal *et al.*[21,22] have shown that $(\bar{\mu}^2/n)^{1/2}/(\bar{\mu}_0^2)^{1/2}$, where $(\bar{\mu}_0^2)^{1/2}$ is the dipole moment of monomer in solution, characterizes the short-range interaction effect and is not affected by long-range interactions. The quantity is also independent of the polarity and quality of the solvent. We studied the quantity $(\bar{\mu}/n)^{1/2}/(\bar{\mu}_0^2)^{1/2}$ for characterization of the free rotation restriction in the polymer chain. Data are shown in *Table 2*. The obtained values of $(\bar{\mu}^2/n)^{1/2}/(\bar{\mu}_0^2)^{1/2}$ change very much, i.e. decrease with increase of temperature. It obtains a value of 1 at a

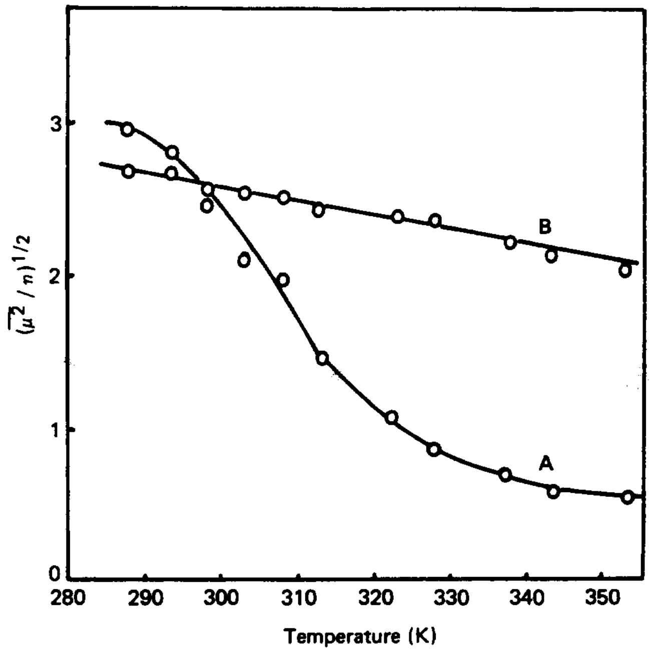

Figure 5 Dependence of the dipole moment of PPhMA (curve A) and PhMA (curve B) on temperature of solution

temperature of about 298 K. In agreement with the theory of this quantity[23] the polymer molecule of PPhMA at this temperature is freely rotating without any restriction.

To calculate the dipole moment of a freely rotating polymer chain of PPhMA, the equation obtained from Kuhn's statistical theory[24] with fixed valence angles of main chain bonds and free rotation around them was used in the following form:

$$\bar{\mu}^2 = nm^2\left(1 - 2\frac{\cos\alpha\cos\beta_1\cos\beta_2}{\sin^2\alpha}\right) \qquad (6)$$

where β_1 and β_2 are the angles between the direction of the dipole and the two C–C bonds attached to it. It is known that for chains of type $\text{-(}CH_2\text{-}CHR\text{)}_n$ with tetrahedral valence angles[20] $\bar{\mu}^2 = 11/12nm^2$ (ref. 23).

In the real polymer molecules, internal rotation is more or less restricted. The dipole moment of a unit of the freely rotating polymer chain calculated using equation (6) equals 2.43 D. For this calculation the dipole moment of monomer $m = 2.54$ D was used and $n = 2170$. The excellent agreement between the calculated and experimental values obtained at 298 K (column 2) is probably better than should be expected. This result suggests that this temperature of about 298 K is the transition temperature for the solution of the PPhMA in dioxane when the attraction and the repulsion of the distant parts of the polymer chain compensate each other completely. At higher temperature the quantity $(\bar{\mu}^2/n)^{1/2}/(\bar{\mu}_0^2)^{1/2}$ decreases very much up to 0.25 at 353 K.

A similar transition in the temperature-dependent behaviour of the dipole moment of poly(methyl acrylate) in benzene solution was found by Masegosa *et al.*[25] and earlier for poly(methyl methacrylate) in toluene solution[26].

CONCLUSIONS

All the measurement methods which were used to study the conformation transition of poly(phenyl methacrylate) in solution suggest the transition between two intramolecular states characterized by different short-range interactions. This conclusion, above all, is confirmed by the significant jump in density dependence on temperature (*Figures 1* and *2*) predicted by the statistical theory of second-order transitions. The observed transition phenomena undoubtedly appear as transitory (belonging to a region of temperature) perturbations of the specific volume with temperature. Some explanation of the nature of the intramolecular interactions is given by the dipole moment studies. The observed strong compensation of the dipole moments in the polymer macromolecule is possible in the presence of specific interactions of phenyl rings. When the phenyl rings of the adjacent units of the chain are interacting, forming the associated dimer (observed in the fluorescence studies[8]), the most probable geometry of the dipole groups of the polymer (carbonyl groups) leads to compensation of the dipole and macroscopically to decrease in the dipole moment of the macromolecule. Our studies of this transition of PPhMA in solution by different methods and with different solvents and the intramolecular nature of this transition confirm our suggestions that this is a thermally induced transition. However, we expect that the nature of this transition and the temperature (i.e. the interval of temperature) should not be very different in bulk, similar to the observations for polystyrene. Further experiments are necessary in order to obtain some definite conclusions about this conformational transition.

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