solutions. Therefore it may be concluded that A_2 is equal to zero independently of the polymer concentration. It has almost been established that A_2 equals zero in the bulk polymer[4,5]. From the data of the osmotic pressure[14], the third virial coefficient A_3 is estimated to be 3.5×10^{-4} cm^{6}g^{-3}mol, despite the prediction by the two parameter theory[18] that $A_3 \rightarrow 0$ as $A_2 \rightarrow 0$. On the other hand, no effect of A_3 on the chain dimensions in θ-solvents at infinite dilution has been found, because the frequency of three-body contacts among the polymer segments is negligibly small. In concentrated solutions, however, the three-body contacts become frequent, which may affect the polymer chain dimension. Nevertheless, the result obtained in this work indicates that the chain dimension remains unchanged in concentrated solutions. From this fact, it may be suggested that A_3 diminishes with increasing polymer concentration, and that the effect of increasing frequency of the three-body contacts is compensated by the decrease of A_3 with increasing concentration.

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Chain flexibility of poly(phenyl thiolmethacrylate)

In spite of the abundant literature published in recent years on the solution properties of polyacrylates and polymethacrylates, the corresponding sulphur containing polymers (thiolacrylates and thiolmethacrylates) have received no attention, although acrylic polymers with sulphur in the side chain possess very good physical properties, e.g. elasticity, stability towards heat and solvents and low degree of swelling[1,2].

Six fractions of poly(phenyl thiolmethacrylate) (PTPH) of M_w from 4.11 $\times 10^4$ to 25.2 $\times 10^4$ were prepared and characterized by light scattering(benzene), viscosity(benzene, methyl ethyl ketone) and gel permeation chromatography (toluene) at 25°C.

The values of K_Θ and of the chain flexibility factor σ are given in *Table 1.* The K_Θ value corrected for polydispersity was obtained as previously[3] using the weight-average molecular weights and the intrinsic viscosities. The value of σ was calculated by taking for Φ the theoretical value of 2.87×10^{21}. In the same Table are given the corresponding values found for poly(phenyl methacrylate) (PPH)[4,5].

Table 1 K_Θ value and chain flexibility factor σ for poly(phenyl thiolmethacrylate) and poly(phenyl methacrylate) at 25° C

Polymer—solvent	$K_\Theta \times 10^3$ (cm^3/g)	σ
Poly(phenyl thiolmethacrylate)		
Benzene		
Methyl ethyl ketone	39.5	2.26
Poly(phenyl methacrylate)[3,4]		
Benzene		
Methyl ethyl ketone	59	2.46

It is clear that the flexibility of PTPH ($\sigma = 2.26$) is much higher than that of PPH ($\sigma = 2.46$). This difference mainly arises from the change in the local intramolecular interactions caused by the substitution of the oxygen atom in PPH by a sulphur atom; the higher flexibility of the sulphur containing side group of PTPH, due to the decrease in the energy barrier around C—S bond[6], seems to contribute also to it.

It is interesting to note, that the difference in the flexibility factors between PTPH and PPH is of the same order as in the case of poly(propylene oxide) ($\sigma = 1.62$) and poly(propylene sulphide) ($\sigma = 1.49$)[7], where the substitution of oxygen by sulphur is in the main chain.

Further investigations on the influence of sulphur-containing side groups on the chain flexibility are in progress.

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