Conformational transitions in poly(butyl methacrylate)

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SUMMARY

Temperature dependence of viscosity data was investigated on poly(butyl methacrylate) fractions in dilute solution. A discontinuity in intrinsic viscosity was observed in the 25°C-35°C temperature range. Sharp changes of unperturbed dimensions were visualized from this behaviour. The phenomenon can be accounted for by assuming conformational changes of the chain in different solvents.

INTRODUCTION

Different papers have appeared, last years, on conformational transitions of synthetic macromolecules (e.g., 1-5). The proposed explanation of the observed transitions was a difference in mobility of the side groups of the chain, below and above the transition temperature.

The present paper is concerned with some viscometric results obtained with poly(butyl methacrylate) (PBuMA) fractions in different solvents as a function of temperature and polymer molecular weight.

EXPERIMENTAL

PBuMA samples were prepared by radical polymerization, by use of various initiator (2,2'-azo-bis-isobutyronitrile) concentrations (0.05-0.2%) at 70°C. The polymer was purified by reprecipitation from acetone solution using aqueous methanol as precipitant, and was finally dried in vacuum at 40°C.

Polymer fractionation was performed by use of acetone--methanol solvent/nonsolvent mixtures.

Molecular weights were determined by use of the Mark--Houwink relation $[\eta] = 0.974 \cdot 10^{-4} \bar{M}_w^{0.68}$ (methyl ethyl ketone (MEK), 25°C) (6).

Intrinsic viscosities $(dl \cdot g^{-1})$ were measured in MEK, benzene (B), cyclohexane (C) and dioxane (D), using an Ubbelohde suspended-level viscometer. The investigated temperature range extended from 15°C to 45°C. The intrinsic viscosities were determined from the Huggins, Kraemer, Martin, Schulz-Blaschke and Fedors equations, and were obtained with an accuracy of the order of 1%.

PBuMA fractions characterized by viscometry were compared to a PBuMA fraction ($\bar{M}_w = 15.07 \cdot 10^6$, light scattering)

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separated from a sample obtained by plasma-induced polymeri-
zation (7-9).

RESULTS AND DISCUSSION

The intrinsic viscosity dependence on temperature for
the studied PBuMA fractions in MEK, B, C and D is shown in
Figure 1. All fractions show a minimum in intrinsic viscosity
in the 25°C-35°C temperature range, minimum less observable
in MEK. The discontinuities in the viscosity as a function of
temperature have been interpreted in terms of conformational
changes of the polymer chain (1, 10); therefore, it can be
considered that PBuMA undergoes a conformational change at
about 30°C.

The phenomenon was also analysed considering the influ-
ence of the solvation power of the solvent. The solvents used
in the present study are cyclic and non-polar (B), cyclic and
polar (C,D), and acyclic and polar (MEK), so that the ques-
tion whether the geometry of the solvent molecules or the
solvent-polymer chain interaction is more relevant cannot be
answered.

Using the viscometric results obtained with the low mo-
lecular weight PBuMA fractions and the relation /1/ (11), the
unperturbed dimensions of the polymer in the solvents, at
various temperatures, can be calculated:

$$1/[\eta] = -A_2 + 1/K_\theta \cdot M^{1/2} \qquad\qquad /1/$$

where $A_2 = 0.51\emptyset_0 BA_1^2$, $\emptyset_0$ being the Flory viscosity constant
and B the Stockmayer-Fixman parameter. The inverse of the
slopes of the obtained straight lines gives the unperturbed
dimensions parameter (K_θ). The variation of K_θ (as determined
by the least squares method) with temperature is presented in
Figure 2.

At the transition point (about 30°C) one can observe a
decrease of the unperturbed dimensions of the polymer, which
means that the macromolecular coils become more flexible.
The decrease is more pronounced in C and D (cyclic, polar
solvents) as compared to MEK (acyclic, polar), and less pro-
nounced in B (cyclic, non-polar) as compared to C or D (cyc-
lic, polar solvents). One can consider that, for the confor-
mational transition to occur, it is necessary for the macro-
molecular chain to reach an energy level such that carbon
atoms can overcome the potential barrier and rotate around
the valence cones. This energy state can be attained in dif-
ferent ways, e.g., temperature or solvent power (1).

In an attempt to interpret the effect of the solvent on
the unperturbed dimensions of macromolecular coils, Orofino
(12), considering polystyrene, grouped the solvents according
to their geometry and proposed an explanation suggesting that
acyclic solvents (e.g., MEK in the present study) allow the
chain to assume conformations involving segment-segment pro-
ximity; on the contrary, this cannot be attained in cyclic
solvents (e.g., B, C, D in this study). From this point of
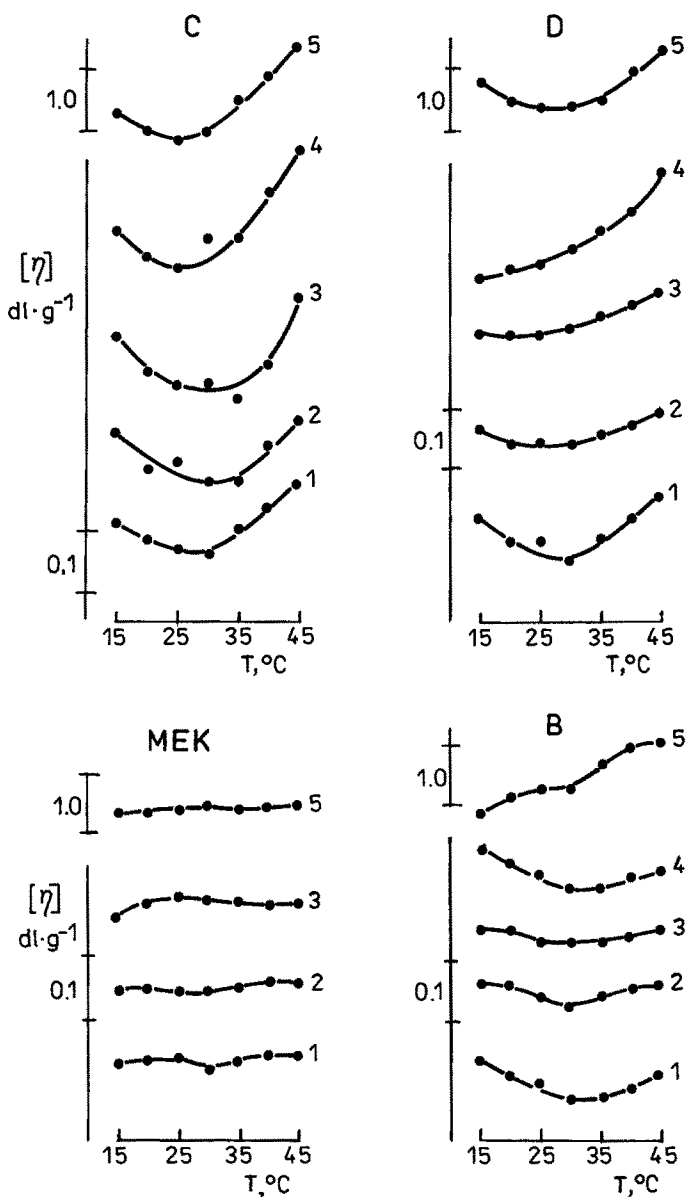view it appears that in MEK the PBuMA chain presents a more

Figure 1. Variation of intrinsic viscosity with temperature for PBuMA fractions in MEK, B, C and D.
1 - $\bar{M}_w = 4.09 \cdot 10^5$, 2 - $\bar{M}_w = 5.71 \cdot 10^5$, 3 - $\bar{M}_w = 9.23 \cdot 10^5$, 4 - $\bar{M}_w = 12.73 \cdot 10^5$, 5 - $\bar{M}_w = 15.07 \cdot 10^6$.

stable conformation as a function of temperature. Considering the behaviour given in Figure 2 from the point of view of solvent polarity, the conclusions become inconsistent.
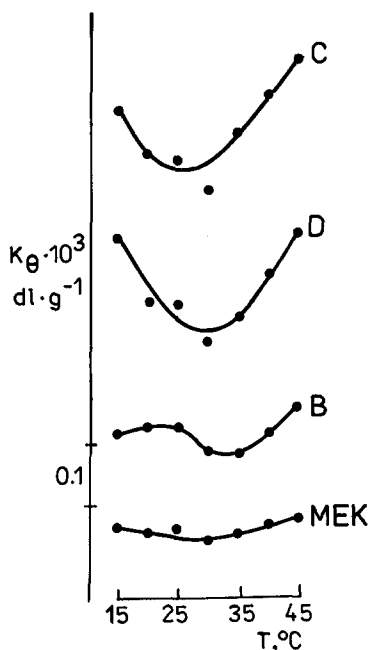
However, the results of the present investigation show that the behaviour of polymer chain in the solvents, as a function of temperature, is determined by both the geometry and the polarity of the solvent, with additive and/or compensative contributions (13).

Table 1 gives the present as well as literature data, summarized by Gargallo et al. (10), on the transition interval ΔT of some polymethacrylates.

The data reported in this study are in agreement with literature conclusions (10) which show that for polymers with bulky side groups the energy required for the occurence of conformational changes is smaller, and thus the transition interval ΔT is lowered.

Apparently, the molecular weight of the sample has no influence on the transition interval as concerns both the magnitude of the effect and the localization. However, systematic studies have to confirm such an observation.

Figure 2. Temperature dependence of the unperturbed dimensions parameter K_θ for PBuMA in MEK, B, C, D.

Table 1
Influence of the nature of the side group on the conformational transition interval ΔT of some polymethacrylates (from viscometric measurements)[a]

Polymer	ΔT ($^{\circ}C$)	Side-group
poly(methyl methacrylate)	45-55	$-CO-O-CH_3$
poly(ethyl methacrylate)	40-45	$-CO-O-CH_2-CH_3$
poly(butyl methacrylate)[b]	25-35	$-CO-O-(CH_2)_3-CH_3$
poly(isobutyl methacrylate)	20-35	$-CO-O-C(CH_3)_2-CH_3$
poly(cyclohexyl methacrylate)	10-30	$-CO-O-C_6H_{11}$
poly(cyclohexylmethyl methacrylate)	5-15	$-CO-O-CH_2-C_6H_{11}$
poly(4-tert-butylcyclohexyl methacrylate)	5-15	$-CO-O-C_6H_{10}-C(CH_3)_2-CH_3$

[a] ref. (10)
[b] this work

CONCLUSIONS

Viscometric studies on PBuMA samples in MEK, B, C and D
at 15°C-45°C allow the following conclusions:
- For all solvents used, conformational transitions
appear in the 25°C-35°C temperature range;
- The classification of solvents according to their geo-
metry and to the polarity doesn't entirely justify the modi-
fication of chain dimensions as a function of temperature,
i.e., ΔK_θ at the transition temperature; the geometry of the
solvent can explain, in part, the observed behaviour, but
considering only the polarity of the solvent, the conclusions
are contradictory. The existence of some cumulative effects
determining the solution behaviour of PBuMA as a function of
temperature has to be supposed;
- The conformational transition interval determined for
PBuMA is in agreement with literature data on different poly-
methacrylates;
- Apparently, the molecular weight of the polymer sample
has no influence on the transition interval.

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