Die Makromolekulare Chemie **176**, *1481–1488 (1975)*

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Molecular Dimensions of Polymers Dissolved in Binary Mixtures of Polar and Non-polar Solvents, 2*)

Poly(methyl methacrylate)

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(Date of receipt: August 5, 1974)

SUMMARY:

Viscometric measurements are performed for poly(methyl methacrylate) fractions dissolved in the following solvent mixtures: benzene/chloroform, benzene/tetrahydrofuran, benzene/ethyl acetate, and dioxane/chloroform. The polymer exhibits a conformational transition which occurs in a narrow region of solvent composition. This transition is expressed by a discontinuity of the intrinsic viscosity, Huggins' constant, and the unperturbed dimensions.

At the transition point all solvent mixtures present approximatively the same dielectric constant.

ZUSAMMENFASSUNG:

Mit Polymethylmethacrylat-Fraktionen wurden in folgenden Lösungsmittelgemischen viskosimetrische Messungen durchgeführt: Benzol/Chloroform, Benzol/Tetrahydrofuran, Benzol/Äthylacetat und Dioxan/Chloroform. Das Polymere zeigt dabei eine Konformationsänderung in einem engen Bereich der Lösungsmittelzusammensetzung. Dieser Übergang äußert sich in einem Sprung des Staudingerindex, der Huggins'schen Konstante und der ungestörten Dimensionen.

Alle Lösungsmittel haben in dem Bereich, in dem dieser Übergang beobachtet wird, nahezu die gleiche Dielektrizitätskonstante.

Introduction

The conformational transitions of poly[1-(methoxycarbonyl)-1-methylethylene], poly(methyl methacrylate), (PMMA), were the subject of two recent

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*) Part 1: cf.[3].

papers. The first[1] deals with the transition of PMMA, dissolved in a single solvent, which occurs when the temperature is changed. The second[2] deals with the transition of PMMA, dissolved in a binary solvent mixture, which occurs when the composition of the solvent mixture is changed.

In this paper, we present a systematic viscometric study of the conformational transitions of the PMMA which was dissolved in a series of various binary solvent mixtures, consisting of a polar and a non-polar solvent. A respective recent study[3] has shown that a conformational transition of poly(2-vinylpyridine) also occurs when this polymer is dissolved in a binary mixture of a polar and a non-polar solvent.

From our results we conclude that all the binary mixtures of a non-polar and a polar solvent used exhibit the same dielectric constant at the point where the transition occurs.

Experimental Part

The samples of PMMA used in this work are fractions of a polymer prepared by anionic technique at low temperature, using THF as solvent.

It is assumed that the PMMA prepared by this method does not present any significant stereoregularity. The molecular weight (M_w) of each fraction was determined by light scattering and their polydispersity (M_w/M_n), determined by gel permeation chromatography, does not exceed the value of 1,2.

The solvents used were p.a. liquids (Merck). The solvent mixtures were always prepared before addition of the polymer, and their composition was expressed by volume fraction.

The intrinsic viscosity was determined under constant pressure using a modified Ubbelohde viscometer, and is given in cm^3/g. In repeated experiments, the error of the intrinsic viscosity $[\eta]$ does not exceed $\pm 1\%$.

It is noticeable that the transition phenomenon did not occur if the polymer or the solvents had absorbed even a small amount of humidity.

Results

The experimental results obtained with various fractions of poly(methyl methacrylate) (PMMA), dissolved in four solvent mixtures are presented below.

Benzene/chloroform

The evolution of the intrinsic viscosity $[\eta]$ of four fractions of PMMA has been studied in this mixture from pure benzene (non-polar solvent) to pure $CHCl_3$ (polar solvent). All fractions show a discontinuity of the evolution of the $[\eta]$ value which starts in a solvent mixture containing 40% $CHCl_3$ by volume.

Fig. 1 shows the variation of $[\eta]$ for one fraction of PMMA ($M_w = 435000$) at two different temperatures. The other three fractions, studied in this mixture, have the following molecular weights: 30000, 130000, and 180000. The unperturbed dimensions of PMMA were determined by the *Stockmayer-Fixman* graphical representation[4] using the value of $[\eta]$ obtained for the four fractions. Thus, the value of $[\eta]/M_w^{1/2}$ is plotted as a function of $M_w^{1/2}$ for all the fractions of PMMA, dissolved in pure benzene, pure chloroform and some mixtures of these two solvents. The straight lines obtained were extrapolated

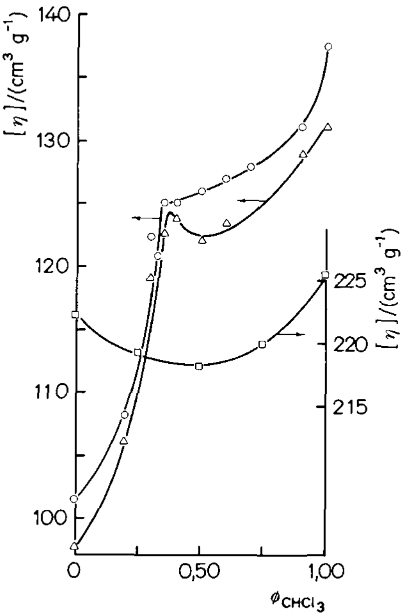

Fig. 1

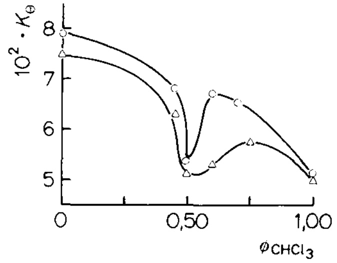

Fig. 2

Fig. 1. Variation of intrinsic viscosity $[\eta]$ for a fraction of PMMA ($M_w = 435000$), dissolved in the binary solvent mixture benzene/$CHCl_3$, as a function of solvent composition expressed as volume fraction of $CHCl_3$ ϕ_{CHCl_3}; (○: 25 °C, △: 55 °C) □: PS in the same mixture at 25 °C

Fig. 2. Variation of K_Θ from *Stockmayer-Fixman* plot[4] for PMMA dissolved in the binary solvent mixture benzene/$CHCl_3$ as a function of solvent composition, expressed as volume fraction of $CHCl_3$, ϕ_{CHCl_3}, at 25 °C (○) and 55 °C (△)

to $M_w^{1/2}$ equal to zero and the intercept of each line with the ordonate then gives the unperturbed dimensions parameter $K_\Theta = [\eta]_\Theta / M_w^{1/2}$.

Fig. 2 gives the variation of the parameter K_Θ of PMMA in passing from pure benzene to pure chloroform, at two different temperatures (25 °C and 55 °C). The observed sharp discontinuity in the variation of the K_Θ value is more important than that observed in the case of $[\eta]$. It should be noted that the phenomenon of the conformational transitions of a polymer deals with the unperturbed dimensions much more than the overall dimensions of the macromolecular chain[3]. This means that the transition of PMMA is the result of an important modification in the short-range interactions. However, as in the case of poly(2-vinylpyridine)[3] the long-range interactions are also affected at the transition point. These interactions are expressed by the parameter B which is obtained by the slope of the Stockmayer-Fixman plot.

The solvent mixture benzene/chloroform is characterized by a negative value of the excess free enthalpy of mixing (ΔG^E)[5]. According to our previous results[6-8] the values of $[\eta]$ for PMMA in this mixture might present a negative deviation in passing from the one to the other pure solvent. As it is shown in Fig. 1, the value of $[\eta]$ for PMMA exhibits a positive deviation. This discrepancy must be attributed to the transition, presented by the polymer in this solvent mixture. On the other hand, the polystyrene, which does not present the transition phenomenon, confirms our proceeding results and gives a negative deviation for the values of $[\eta]$ in the same solvent mixture (cf. Fig. 1).

Benzene/tetrahydrofuran

The variation of $[\eta]$ of one fraction of PMMA ($M_w = 435000$) was studied in this mixture as a function of solvent composition. It is seen in Fig. 3 that the dimensions of the polymer, expressed by $[\eta]$ exhibit a discontinuity which is much more marked when the measurements are performed at 55 °C.

It is of interest that the quantity of benzene in this mixture, at the transition point, is very different from that in the benzene/chloroform mixture.

The variation of Huggins' constant k', obtained by viscometric measurements, as a function of the solvent composition is given in Fig. 4. The value of k' shows a discontinuity as the value of $[\eta]$, and in the same region of the composition of the solvent mixture.

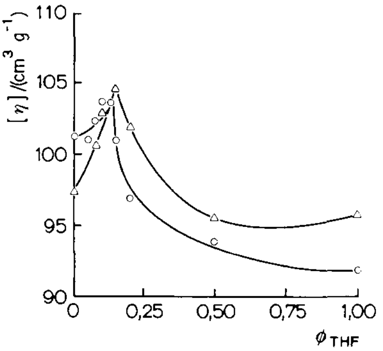

Fig. 3

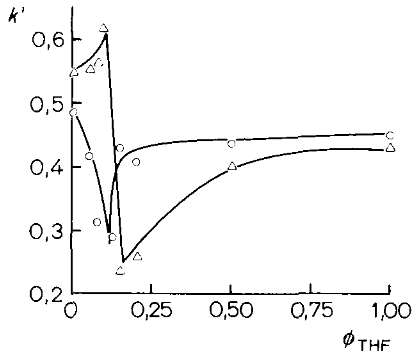

Fig. 4

Fig. 3. Variation of intrinsic viscosity $[\eta]$ for a fraction of PMMA ($M_w = 435000$), dissolved in the binary solvent mixture benzene/THF, as a function of solvent composition, expressed as volume fraction of THF, ϕ_{THF}, at 25 °C (○) and 55 °C (△)

Fig. 4. Variation of Huggins' constant k' for a fraction of PMMA ($M_w = 435000$), dissolved in the binary solvent mixture benzene/THF as a function of solvent composition, expressed as volume fraction of THF, ϕ_{THF}, at 25 °C (○) and 55 °C (△)

Benzene/ethyl acetate

The variation of $[\eta]$ of two fractions of PMMA ($M_w = 250000$ and $M_w = 509000$) was studied in the solvent mixture benzene/ethyl acetate as a function of the solvent composition. A discontinuity in the variation of $[\eta]$ is shown in Fig. 5 which corresponds to a mixture containing 20% benzene by volume.

Dioxane/chloroform

In the mixture dioxane/chloroform, dioxane is considered as the nonpolar solvent and chloroform as the polar solvent. PMMA shows even in this mixture a transition which occurs if the mixture contains 40% chloroform (Fig. 6).

The mixture dioxane/chloroform is characterized by a high negative value of ΔG^{E}[9] and according to our previous results[6–8] polystyrene shows a high negative deviation of $[\eta]$ (Fig. 6). PMMA exhibits a lower negative deviation which must be attributed to the transition phenomenon.

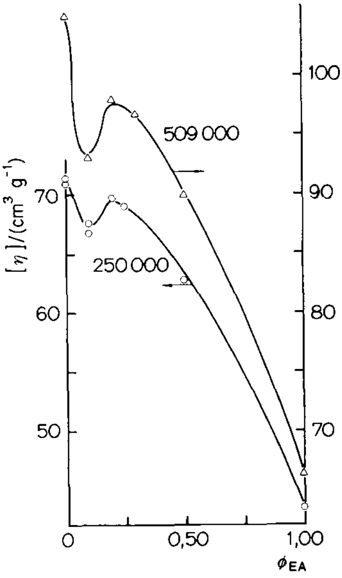

Fig. 5

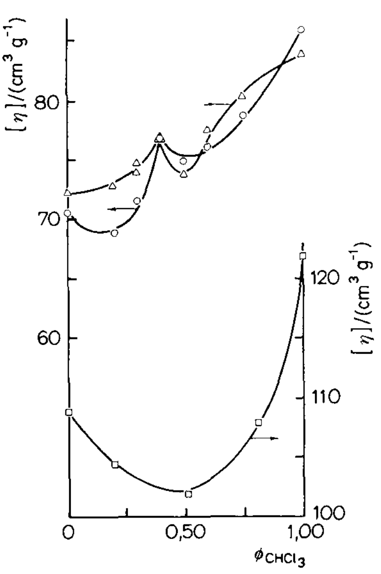

Fig. 6

Fig. 5. Variation of intrinsic viscosity $[\eta]$ for two fractions of PMMA, dissolved in the binary solvent mixture benzene/ethyl acetate, as a function of solvent composition, expressed as volume fraction of ethyl acetate, ϕ_{EA}, at 25 °C; $M_w = 250000$ (○), $M_w = 509000$ (△)

Fig. 6. Variation of intrinsic viscosity $[\eta]$ for a fraction of PMMA ($M_w = 250000$), dissolved in the binary solvent mixture dioxane/$CHCl_3$, as a function of solvent composition, expressed as volume fraction of $CHCl_3$, ϕ_{CHCl_3}; (○: 25 °C, △: 55 °C) □: PS in the same mixture at 25 °C

Discussion

It has been shown that some polymers exhibit a different viscometric behaviour depending on the solvent (good or poor) in which they are dissolved. This effect is explained by different configurations of the same polymer[10,11] and by different displacement lengths of the chain[12].

In order to explain our results, we assume the non-polar solvent to be the poor one and the polar solvent to be the good one. We can accept that the polymer chain contains some ordered sequences when it is dissolved in a non-polar solvent. This ordered structure is stabilized by the interactions between the side groups and the adequate environments of the chain by the molecules of the non-polar solvent. If the polymer is dissolved in a polar solvent the environments of the chain by the molecules of this solvent would be different and the ordered structure would also be different, since the rôle of the solvent during the formation of the ordered structure is very important[13,14].

According to the above considerations, we can say that the transition phenomenon, studied in this work is the result of a change of the structure of PMMA by a cooperative phenomenon. In other words, at the transition point, we have a passage from an ordered structure of the polymer, stable in the non-polar solvent, to another ordered structure stable in the polar solvent. In the narrow region of composition of the solvent mixture in which the transition occurs, the macromolecular chain exhibits a very disordered structure which is characterized by a decrease of the unperturbed dimensions as it is shown in Fig. 2.

The previous data have led us to the conclusion that all the binary solvent mixtures have approximatively the same dielectric constant (ε) at the point where the transition of the PMMA occurs. As Tab. 1 shows, the values of ε for the different mixtures, which correspond to the transition point, are close one another. This means that the dielectric constant seems to be the parameter, which determines the transition of PMMA when this polymer is dissolved in a mixture of a polar and a non-polar solvent. The difference observed in the values of the dielectric constant may be also due to the non-linear variation of ε in passing from one solvent to the other[15].

It should be noted that the conformational transition of PMMA dissolved in the binary mixture acetone chloroform[2] takes place if this mixture has a value of ε much higher than the values given in Tab. 1. This discrepancy can be explained by the fact that the poor solvent (acetone) in the mixture acetone/chloroform is also a very polar solvent. In other words, the polymer was dissolved in a mixture of two polar solvents.

Tab. 1. Dielectric constant ε of the binary solvent mixtures at the point at which conformational transition of PMMA starts

Mixture composition (by volume)	ε
Benzene/$CHCl_3$ (60:40)	3,20
Benzene/THF (87,5:12,5)	2,90
Benzene/ethyl acetate (80:20)	3,05
Dioxane/$CHCl_3$ (60:40)	3,20

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