Investigation of conformational transitions in bisphenol A poly(carbonate) macromolecules in mixtures of 1,1,2,2-tetrachloroethane and n-propyl alcohol

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The intrinsic viscosity of bisphenol A poly(carbonate) solutions in mixtures of 1,1,2,2-tetrachloroethane and n-propyl alcohol was found to decrease with increasing n-propyl alcohol concentration. A conformational transition was proved to occur within the range 30–40 vol % of n-propyl alcohol. This phenomenon has been studied by viscometric measurements for various n-propyl alcohol concentrations and for polymer samples with different molecular weights. The results were interpreted by assuming that the observed decrease of intrinsic viscosity is due to a conformational transition in the bisphenol A poly(carbonate) macromolecules. An increase in measurement temperature was found to cause a decrease of intrinsic viscosity. This fact was explained in terms of a partial helix–coil conformational transition. By means of a calorimetric method, the heat effects accompanying the conformational transitions of bisphenol A poly(carbonate) in the solution were examined.

(Keywords: bisphenol A poly(carbonate); collapse transition; intrinsic viscosity; chain conformation; helix–coil transition; heat effects; calorimetric method)

INTRODUCTION

Precipitation of polymers from homogeneous solutions, in general phase separation, is a complex process and it goes through a series of intermediate stages[1]. Recent theories treated the precipitation process as composed of two basic stages[2]: the earlier stage, frequently called 'nucleation', occurs by spinodal decomposition or by nucleation and growth[3]; and the latter stage, called 'coarsening'[4], appears to be a gradual phase aggregation of the so-called 'daughter phases'[2,5,6] until the polymer is precipitated or another two-element system formed. The latter stage is generally called the growth stage. However, in the light of recent work on this phenomenon[7,8] as well as our latest research[9], it may be concluded that this process is associated with a conformational transition of the polymer chain taking place in the first stage. Nucleation and growth occurs in the second stage.

In recent years many works have appeared concerning conformational transitions of macromolecules[10,11] in solutions. Nevertheless, many aspects of this phenomenon remain unexplained. The aim of the present work was to study conformational transitions of a polymer chain, accompanying the precipitation of bisphenol A poly(carbonate) from solution. On the basis of literature it was stated that a collapse transition[12,13] or a partial helix–coil transition of the chain[14] could be possible. In order to investigate the problem, viscometric measurements were carried out of bisphenol A poly(carbonate) solutions in tetrachloroethane/1-propanol. Intrinsic viscosities of these solutions were determined as a function of temperature and 1-propanol content. Calorimetric measurements of heat effects accompanying conformational transitions were carried out in order to give a full explanation of these changes.

EXPERIMENTAL

Materials

Bisphenol A poly(carbonate) (hereafter called I) (trade name, Bistan AF), obtained from the Institute of Industrial Chemistry in Warsaw, was the polymer used in the present work. The samples of polymer I had viscosity-average molecular weight $\bar{M}_v = 52\,890$ and $29\,500$ (determined in 1,1,2,2-tetrachloroethane at 25°C) and weight-average molecular weight $\bar{M}_w = 57\,000$ and $32\,000$, respectively. Determinations of weight-average molecular weights were carried out by means of an HSGPC Liquid Chromatograph type 302 (IChF PAN, Warsaw). Separon 50 and Separon 500 columns were used ($2 \times 1250 \times 6$ mm), from Laboratory Instruments Works. The determinations were carried out in solution in tetrahydrofuran (THF) and the calculations of molecular weights were based on the polystyrene scale.

Solvents and solutions

1,1,2,2-Tetrachloroethane (made by POCh, Gliwice) was used as the polymer I solvent. It was purified by distillation under argon, resulting in a colourless liquid with refractive index of $n_D^{20} = 1.4942$.

The precipitating agent, 1-propanol (POCh, Gliwice, Poland), was used without further purification. Research carried out by means of a Varian Gas Chromatograph and n.m.r. proved the precipitating agent to be free from any contamination.

Polymer solutions were obtained by dissolving a suitable amount of the polymer in a given quantity of the solvent or in a suitable mixture of 1,1,2,2-tetrachloroethane/n-propyl alcohol at a suitable temperature in order to study the influence of density and

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concentration changes with temperature, and this was then stored at room temperature. Measurements were carried out after prior heating or cooling of the solution to the required temperature.

Viscometry

Suspended-meniscus Ubbelohde capillary viscometers were used. The viscometric measurements were carried out at 25, 30, 40, 50, 60, 70 and 80°C, the viscometers being immersed in a thermostatted water bath with temperature regulation accuracy of 0.01°C. The Hagenbach–Couette kinetic-energy-loss correction factor was taken into account for each measurement. The values of the correction factors were obtained from correction tables supplied by the manufacturers of the viscometers. The solvents and solutions were filtered through a glass frit (1G-2) before the measurements. The intrinsic viscosity $[\eta]$ was determined from Huggins' plots obtained for 4–5 concentrations in the range $(0.1-10)\times 10^{-3}\,\mathrm{g\,mol^{-1}}$. The quantity $(\eta_r-1)/c$ was determined as a function of polymer concentration c, where η_r is the relative viscosity calculated as t/t_0 (t and t_0 are the efflux times of the polymer solution and solvent, respectively). The value of intrinsic viscosity $[\eta]$ was given by the point of intersection of the respective Huggins' plots with the ordinate. For higher n-propyl alcohol concentrations, solutions with concentrations of polymer $<3\times 10^{-3}\,\mathrm{g\,mol^{-1}}$ were used to avoid the occurrence of aggregation and precipitation phenomena. The values of $[\eta]$ presented in this paper are the mean values obtained for two series of measurements per temperature on PC samples. The accuracy of the viscometric measurement lies within the range of $0.3-0.5\,\mathrm{ml\,g^{-1}}$.

Microcalorimetric measurements

Heat effects of the examined process of polymer precipitation and the effects of mixing the solvent with the precipitating agent were determined by means of a BMR-type non-isothermal non-adiabatic differential microcalorimeter[15] (IChF PAN, Warsaw). After reaching thermal equilibrium the measurements were started on breaking a sealed glass ampoule containing a known amount of bisphenol A poly(carbonate) solution in 1,1,2,2-tetrachloroethane (or pure 1,1,2,2-tetrachloroethane) of a suitable, known concentration placed in the calorimetric cell filled with the precipitating agent (n-propyl alcohol). Concentration of reagents was chosen in such a way that the final polymer concentration would always be identical. The whole contents of the measurement cell was 16 ml. Changes of the thermoelectric force generated by the microcalorimeter thermopile were recorded on an EZ-10 type recorder (Laboratorni Pristroje, Prague, Czechoslovakia). Changes of the thermoelectric force (TEF) are known to represent thermal effects of the process investigated. The amount of heat produced was calculated while measuring the thermoelectric force changes, until the initial value of the thermoelectric force was reached (i.e. zero)[15]:

$$Q(t)\Big|_{t_0}^{t_1} = \alpha \int_{t_0}^{t_1} \theta(t)\,\mathrm{d}t \qquad (1)$$

In this equation $Q(t)\Big|_{t_0}^{t_1}$ is the whole amount of heat evolved in the time interval (t_0, t_1) to TEF zero value at the completion of the measurement, and $\theta(t)$ describes the TEF change with time t_0. The heat loss coefficient $\alpha = 1.702\,\mathrm{J\,mV^{-1}\,min^{-1}}$ was determined experimentally when calibrating the calorimeter[16].

RESULTS AND DISCUSSION

Dependence of the intrinsic viscosity $[\eta]$ of bisphenol A poly(carbonate) solutions in 1,1,2,2-tetrachloroethane/n-propyl alcohol mixtures on n-propyl alcohol concentration for samples with $\bar{M}_w = 32\,000$ and $\bar{M}_w = 57\,000$ is shown in *Figure 1a* and *Table 1*. *Figure 1b* and *Table 1* also show hydrodynamically equivalent radii for these polymer samples.

Hydrodynamically equivalent radii were calculated from intrinsic viscosity values using the equivalent sphere expression for intrinsic viscosity[17]:

$$[\eta] = \frac{(10\pi N_A/3)\bar{R}_e^3}{\bar{M}_w} \qquad (2)$$

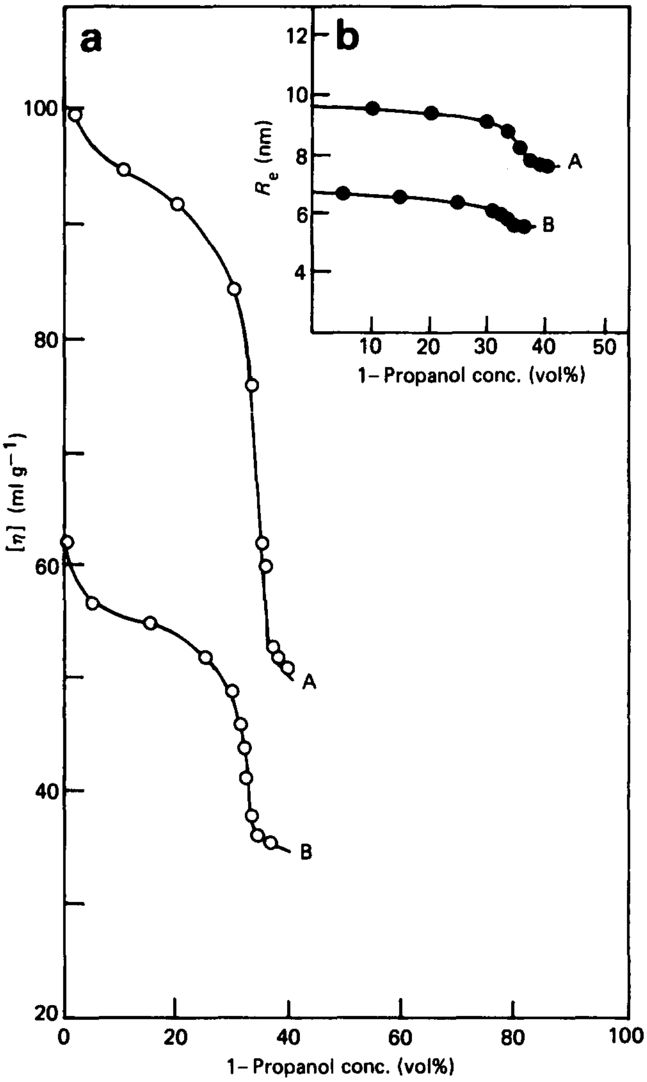

Figure 1 (a) Dependence of the intrinsic viscosity $[\eta]$ of bisphenol A poly(carbonate) solutions in 1,1,2,2-tetrachloroethane/1-propanol mixtures on 1-propanol concentration. (b) Dependence of the hydrodynamically equivalent ratius ($\bar{R}_e$) of bisphenol A poly(carbonate) in these same solutions on 1-propanol concentration. Measurement temperature, 25°C. Weight-average molecular weight: curves A, 57 000; curves B, 32 000

Table 1 Hydrodynamically equivalent radii for bisphenol A poly(carbonate) of $\bar{M}_w = 32000$ and $\bar{M}_w = 57000$ in solutions of tetrachloroethane/n-propyl alcohol mixtures at 25°C

$\bar{M}_w = 32000$			$\bar{M}_w = 57000$		
n-Propyl alcohol concentration (vol%)	[η] (ml g^{-1})	$\bar{R}_e$ (nm)	n-Propyl alcohol concentration (vol%)	[η] (ml g^{-1})	$\bar{R}_e$ (nm)
0	62	6.80	0	100	9.66
5	56.5	6.59	10	95	9.50
15	55	6.53	20	92	9.40
25	52	6.41	30	84.5	9.14
30	49	6.28	33.6	76	8.82
31.2	46.6	6.18	35.31	62	8.24
32	44	6.06	36	60	8.15
32.8	41.2	5.93	37.3	53	7.82
33.6	38	5.77	38.49	52	7.77
34.4	36	5.67	39.0	52	7.77
35.31	36	5.67	40.0	51	7.77

where $\bar{R}_e$ is equivalent radius, N_A Avogadro's number ($N_A = 6.02252 \times 10^{-23}\,\mathrm{mol}^{-1}$) and $\bar{M}$ the molecular weight.

The results of our viscosity measurements (*Figure 1*) indicate a conformational transition. For low n-propyl alcohol concentrations, the intrinsic viscosity [η] and the equivalent radii are large, and in the limiting case of zero n-propyl alcohol concentration these values are equal to 100 ml g^{-1} and 9.668 nm, respectively, for the sample of $\bar{M}_w = 57000$ and 62 ml g^{-1} and 6.801 nm for the sample of $\bar{M}_w = 32000$. With increasing n-propyl alcohol concentration, the values of intrinsic viscosities and equivalent radii decrease. In the region of n-propyl alcohol concentration equal to 30–40 vol%, the curve showing the dependence of intrinsic viscosity [η] on n-propyl alcohol concentration exhibits a sudden decrease in [η] values, which indicates a decrease in the size of the polymer coil. On further increasing the n-propyl alcohol concentration, the intrinsic viscosity remains constant and it is 51 ml g^{-1} and 36 ml g^{-1}, which corresponds to equivalent radii of 7.22 nm and 5.67 nm, for samples with $\bar{M}_w = 57000$ and $\bar{M}_w = 32000$m respectively. The observed drop in intrinsic viscosity value [η] within the whole investigated range of n-propyl alcohol concentrations may be interpreted as a polymer collapse phenomenon. The concentration of 30 vol% of n-propyl alcohol and ~3.5 × 10^{-3} g ml^{-1} of polymer represent the precipitation point at the temperature of 25°C.

By lowering the polymer concentration to $< 3 \times 10^{-3}$ g ml^{-1} it was possible to avoid polymer aggregation and precipitation, thus allowing observation of the changes occurring on further increasing the concentration of the precipitating agent[18–20]. The collapse transition observed here is not a discrete transition, which is caused by a small length of the polymer chain[13]. For the polymer of higher molecular weight $\bar{M}_w$, the viscosity decrease is greater (*Figure 1*) than for the polymer of lower molecular weight, $\bar{M}_w = 32000$. This is in agreement with a theory according to which a chain of infinite length should exhibit a discrete transition[13].

Figure 2 shows the variation of [η] for bisphehol A poly(carbonate) solutions in 1,1,2,2-tetrachloroethane/n-propyl alcohol mixtures, as a function of temperature. The samples had weight-average molecular weight equal to 57 000. The measurements were carried out for solutions with concentrations of 0 and 20 vol% n-propyl alcohol, where the collapse transition had not yet taken place (*Figure 1a*), and for concentrations of 30 and 33.6 vol% n-propyl alcohol, where the collapse transition had already occurred (*Figure 1a*). The results of the viscosity measurements at various temperatures are depicted in *Table 2*. *Figure 2* and *Table 2* show that the intrinsic viscosity decreases with increasing temperature for all poly(carbonate) solutions investigated, and especially for those of 0, 20 and 30 vol% concentrations, which suggests that the size of the polymer coil decreases instead of being expanded[18]. For n-propyl alcohol concentration of 30 vol%, a drop of intrinsic viscosity is observed at the first stage, followed by an increase to a certain value and a repeated drop on further temperature increase. For the solution with 33.6 vol% of 1-propanol, i.e. for the solution in which the conformational collapse transition had been completed (*Figure 1*), a growth of intrinsic viscosity value is observed, until a certain value is reached, and then the value of intrinsic viscosity decreases with further temperature increase.

The decrease of intrinsic viscosity on increasing the temperature has been observed for several other polymers[7,10,11,18,21], but so far no satisfactory explanation has been given. No data may be found in the literature concerning the occurrence of this phenomenon for bisphenol A poly(carbonate). It seems that a conformational transition of the polymer chain in the solution gives a reasonable explanation of the fact

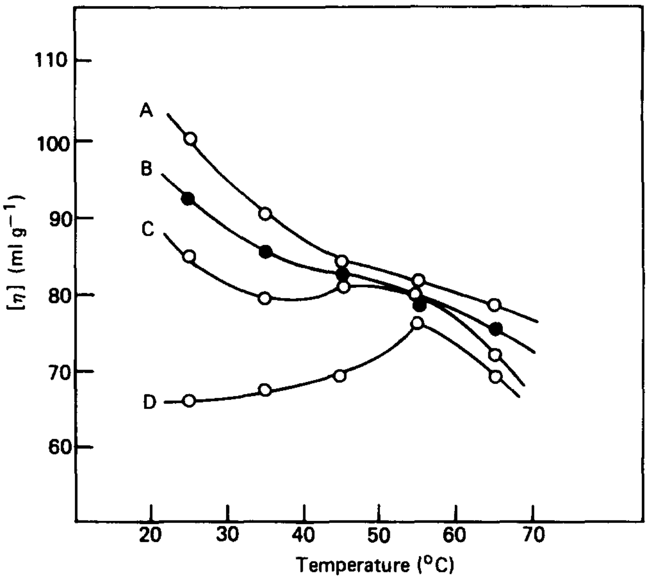

Figure 2 Intrinsic viscosity [η] of bisphenol A poly(carbonate) solutions in 1,1,2,2-tetrachloroethane/1-propanol mixtures as a function of temperature and 1-propanol content: curve A, 0; curve B, 20; curve C, 30; curve D, 33.6 vol%

Table 2 The intrinsic viscosity of bisphenol A poly(carbonate) solutions in 1,1,2,2-tetrachloroethane/n-propyl alcohol mixtures. $\bar{M}_w = 57000$

n-Propyl alcohol concentration (vol%)	[η] (ml g^{-1})					
	25°C	35°C	45°C	55°C	65°C	75°C
0	100	91	84	81.5	78	74
20	92.5	85.5	82.5	79	76	71.5
30	85	79.5	82.0	80	72	
33.6	66	67.5	69.0	76.5	69.5	

observed. To make the statement more precise, it should be said that at lower temperatures strong interactions occur between side groups, resulting in a rather rigid or helical chain structure. Rotations become easier and the rigidity of parts of the polymer chain disappears, the chain becoming flexible and taking a coil form when the temperature rises. In such a case, a temperature rise would result in a decrease in the number of helical sequences (i.e. damage to the helical structure) and thus creation of a more compact coil with its size getting smaller. Hence a decrease in intrinsic viscosity reflects this on a macroscopic scale. In the case of a solution with 33.6 vol% of n-propanol, a growth of intrinsic viscosity (and growth of coil size) with temperature rise might be explained by the fact that at 25°C the polymer in this solution is collapsed (*Figure 1*). A temperature increase would cause an expansion and a transition to a more extended coil conformation of greater size, in which creation of more rigid forms, e.g. helix form, could occur.

The phenomenon of successive viscosity drop (*Figure 2*) may bear witness to this, and supports the hypothesis that a collapse transition may occur in the bisphenol A poly(carbonate) solution under the influence of the precipitating agent.

Tables 3 and *4* and *Figure 3* present the results of investigations concerning thermal effects connected with conformational transitions of a bisphenol A poly(carbonate) chain in solution under the influence of the precipitating agent. The investigations were carried out at 25°C for a polymer of $\bar{M}_w = 57000$. Curve A in *Figure 3* shows the results obtained for the final precipitating mixture at a constant concentration of polymer. Curve B shows the results obtained for the final precipitating mixture at variable polymer concentration. The same figure also presents the course of the collapse transition, depicted by means of the behaviour of the hydrodynamically equivalent radius with respect to solvent concentration. As can be seen the $Q_p - Q_m$ curves of the difference between heat effects of precipitation Q_p and mixing Q_m (of 1,1,2,2-tetrachloroethane with 1-propanol) are similar in shape; for the measurements with a constant polymer concentration, curve A is moved slightly up and leftwards. The curves representing differences between precipitation Q_p and mixing Q_m heats go through a maximum in the concentration range of 90 vol% of 1,1,2,2-tetrachloroethane and then the value of this difference decreases.

Table 3 Differences ($Q_p - Q_m$) as a function of the composition of the precipitating system at a variable polymer concentration ($T = 25$°C). Initial polymer concentration in the solution of 1,1,2,2-tetrachloroethane was $c = 0.006019$ g cm^{-3}, $\bar{M} = 57000$

Precipitating system (vol%)				
TCE	nPA	Q_p (J g^{-1})^a	Q_m (J g^{-1})^a	$Q_p - Q_m$ (J g^{-1})^a
2.66	97.34	23.55	22.12	1.43
6.66	93.34	17.56	17.98	−0.42
15.62	84.38	10.96	11.87	−0.91
20	80	7.88	8.47	−0.59
24	76	5.19	5.28	−0.09
27.58	72.42	3.35	3.51	−0.16
33.57	66.43	0.73	0.82	−0.09
60.0	40	−0.50	−0.52	0.02
70.83	29.17	−1.01	−1.05	0.04
80	20	−1.20	−1.38	0.18
84.28	15.72	−1.52	−1.84	0.32
87.5	15.5	−1.47	−2.07	0.50
90	10	−1.65	−2.25	0.60
93.75	6.25	−1.45	−1.94	0.49
97.41	2.59	−1.5	−1.76	0.26

[a] Measured as joules per gram of 1,1,2,2-tetrachloroethane

Table 4 Differences ($Q_p - Q_m$) as a function of the composition of the precipitating system at constant polymer concentration in the final precipitating mixture of $c = 0.003611$ g cm^{-3} ($T = 25$°C). $\bar{M}_w = 57000$

Precipitating system (vol%)		
TCE	nPA	$Q_p - Q_m$ (J g^{-1})^a
60	40	0.02
70	30	0.44
73	27	0.54
80	20	0.77
85	15	0.71
90	10	0.55
95	5	0.37

[a] Measured as joules per gram of 1,1,2,2-tetrachloroethane

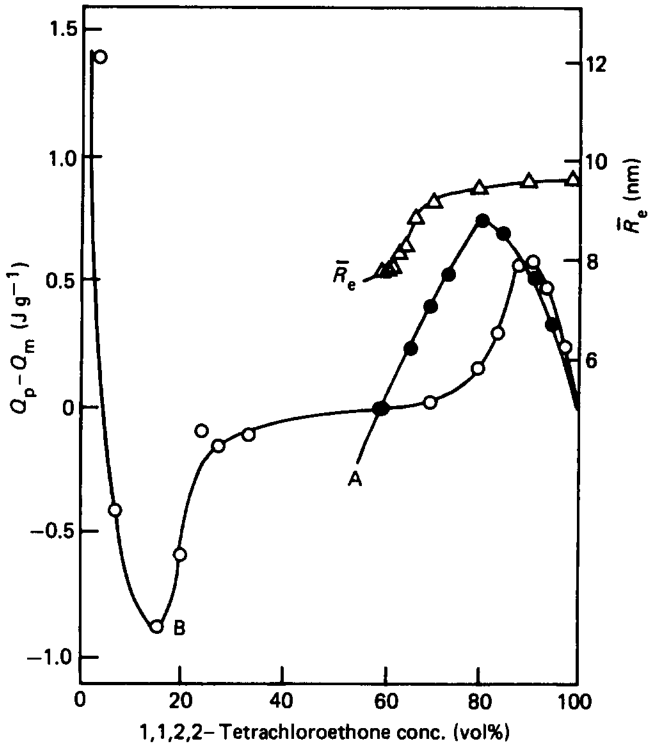

Figure 3 Hydrodynamically equivalent radius $\bar{R}_e$ and the difference ($Q_p - Q_m$) between heats of precipitation (Q_p) of poly(carbonate) and heats of mixing (Q_m) of 1,1,2,2-tetrachloroethane with 1-propanol as a function of the composition of the precipitating system. Measurement temperature, 25°C. $\bar{M}_w = 57000$. Curve A, ($Q_p - Q_m$) at constant concentration of the bisphenol A poly(carbonate) equal to 0.003611 g cm^{-3}. Curve B, ($Q_p - Q_m$) at variable polymer concentration. (Q_p and Q_m are measured in joules per gram of 1,1,2,2-tetrachloroethane)

For the system with variable polymer concentration (curve B), a decrease of $Q_p - Q_m$ to the value of -0.8 J g^{-1} of tetrachloroethane is observed, with an inflection point in the range of 70–60 vol% of 1,1,2,2-tetrachloroethane. This is followed by a growth of this value associated with the increase of the precipitating agent, 1-propanol.

It is known from the literature[17] that the thermal effect of precipitation is expressed by

$$Q_p = -e_{11} + e_{22} - 2e_{21} - e_{33} + 2e_{31} \tag{3}$$

where e_{11}, e_{22}, e_{21}, e_{33} and e_{31} are the energies of mutual molecular interactions of the solvent, of the polymer, of the solvent and polymer, of the precipitator, and of the precipitator and solvent, respectively.

The heat of mixing of precipitating agent with the solvent may be expressed as:

$$Q_m = -e_{11} - e_{33} + 2e_{31} \qquad (4)$$

The difference between the heat of precipitation and the heat of mixing gives the relation

$$Q_p - Q_m = -2e_{21} + e_{22} \qquad (5)$$

The precipitation may be interpreted as a process connected with the change in number of bonds between the units of the polymer chains and the bonds between the polymer and the solvent molecules. The $Q_p - Q_m$ difference may be treated as a measure of the conformational transitions of the polymer in solution. Within the concentration range of 0 to 20 vol % of 1,1,2,2-tetrachloroethane, the macromolecules of the polymer occur in the more compact conformation. The increase of the amount of solvent from 0 to 20 vol % causes the polymer coil to unfold into a looser conformation coil in the precipitated polymer, thus giving an increase in the e_{21} value and therefore a decrease in the value of $Q_p - Q_m$ (*Figure 3*, curve B).

The difference $Q_p - Q_m$ rises with further growth of the solvent content in the solution to 88 vol % for curve B and for the solvent concentrations from 60 to 80 vol % for curve A, although the polymer concentration is constant in the case of curve A. This probably results from changes in the conformation of macromolecules, e.g. creation of helical structures proved previously. It causes a growth of the e_{22} value (energy of mutual polymer–polymer interaction) in equation (5) and a decrease of the e_{21} value (energy of polymer–solvent interactions).

The onset of precipitation at the temperature of 25°C corresponds to a 30 vol % n-propyl alcohol concentration in the precipitation mixture.

The position of $Q_p - Q_m$ value for 60 vol % of 1,1,2,2-tetrachloroethane corresponds to the end of the collapse transition determined by the viscometric method. (*Figure 3*, $\bar{R}_e$ curve). Measurements of the hydrodynamically equivalent radius were carried out until a certain concentration of precipitating agent was reached, as was mentioned above (because of the dilution being too great and the too unsatisfactory measurement precision connected with it). Together with further growth of 1,1,2,2-tetrachloroethane concentration, a decrease of $Q_p - Q_m$ is observed, which results from an increase of the e_{21} value responsible for the growth of polymer–solvent interactions (the growth of the e_{21} segment is caused by greater solvation or increase of the 'goodness' of the solvent, because of the decrease of the precipitating agent concentration). It causes further expansion of the coil towards a more rigid structure, which is shown by temperature investigations of the intrinsic viscosity. It results in a decrease of the e_{22} segment and an increase of the e_{21} segment; hence the difference of heat effects $(Q_p - Q_m)$ decreases.

REFERENCES

1 Milhofer, H. F. *Pure Appl. Chem.* 1981, **53**, 2041

2 Siggia, E. D. *Phys. Rev.* 1979, **A20**, 595

3 Cahn, J. W. *Trans. Metall. Soc. AIME* 1968, **242**, 166

4 Zarzycki, J. *Disc. Faraday Soc.* 1971, **50**, 122

5 Lifshitz, J. M. and Slyozov, V. V. *J. Phys. Chem. Solids* 1961, **19**, 35

6 Wagner, C. *Z. Elektrochem.* 1961, **65**, 581

7 van den Berg, I. W., van de Ridder, G. and Smolders, C. A. *Eur. Polym. J.* 1981, **17**, 935

8 Koenhen, D. M. and Smolders, C. A. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 155, 167

9 Janeczek, H. and Turska, E. *Polymer* 1983, **24**, 1590; *Acta Polym.* 1985, **3**, 144

10 Tsitsilianis, C., Pierri, E. and Dondos, A. *J. Polym. Sci., Polym. Lett. Edn.* 1983, **21**, 685 and references therein

11 Katime, J., Ibarra, X., Garay, M. and Valanciano, R. *Eur. Polym. J.* 1981, **17**, 509 and references therein

12 Williams, C., Brochard, R. and Frisch, H. L. *Annu. Rev. Phys. Chem.* 1981, **32**, 433 and references therein

13 Sanchez, J. C. *Macromolecules* 1979, **12**, 980

14 Fuji, M., Nagasaka, K., Shimada, J. and Yamakawa, H. *Macromolecules* 1983, **16**, 10

15 Zielenkiewicz, A. *Bull. Acad. Pol. Sci. Ser. Sci. Chem.* 1973, **21**, 333

16 Turska, E. and Janeczek, H. *Polymer* 1978, **19**, 81

17 Morawetz, H. 'Macromolecules in Solution', 2nd Edn., Wiley, New York, 1975

18 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953

19 Swislow, G., Sun, S. T., Nishio, I. and Tanaka, T. *Nature* 1979, **281**, 5728

20 Nierlich, M., Cotton, J. P. and Farnoux, B. *J. Chem. Phys.* 1978, **69**(4), 15

21 Tuzar, Z., Kratochwil, P. and Bohdanecky, M. *Adv. Polym. Sci.* 1979, **30**, 117