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Dissolution behavior and solution properties of polyvinylalcohol as determined by viscometry and light scattering in DMSO, ethyleneglycol and water

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Abstract

As it is very difficult to obtain molecularly dispersed solutions of polyvinylalcohol (PVA) in water and as the properties of these solutions change on ageing due to the formation of aggregates, the dissolution behavior and solution properties of PVA with molar masses ranging from 15 to 690 kg/mol in two other solvents, dimethylsulfoxide (DMSO) and ethyleneglycol (EG) was investigated by continuously monitoring η_{sp}/c as a function of dissolution time using a simple Ubbelohde viscometer and light scattering. The optimum dissolution temperatures ranged from 60 to 120°C. The solutions remain stable for at least 24 h. Even yarns which are virtually insoluble in water could successfully be dissolved in DMSO at 120°C. The Huggins constant for PVA both in water and ethyleneglycol is 0.5 and 0.3 in DMSO. Filtration of the PVA solutions in DMSO caused no clogging of filters (0.2 μm). From light scattering it became apparent that PVA is molecularly dispersed in DMSO and that the solutions show no aggregation and hence no ageing. For PVA in DMSO the second virial coefficient appeared to be $4\text{–}15 \times 10^{-4}$ cm^3 g^{-2} mol. This may be compared to $<2 \times 10^{-4}$ cm^3 g^{-2} mol in water. The Mark–Houwink relations for PVA in DMSO at 65°C ($[\eta] = 1.51 \times 10^{-4}\ M_w^{0.804}$), ethyleneglycol at 140°C ($[\eta] = 3.54 \times 10^{-4}\ M_w^{0.692}$) and water at 30°C ($[\eta] = 6.51 \times 10^{-4}\ M_w^{0.628}$), were established. These findings indicate that DMSO is a good solvent for PVA. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Molecular characterization; Ageing; Aggregation

1. Introduction

Polyvinylalcohol (PVA) has important commercial applications [1–3]. This is attributable to the high melting temperature, and polar properties. Characterization of the molecular structure of PVA in terms of intrinsic viscosity, average molar mass or molar mass distribution (MMD) is mostly performed using water as the solvent. In order to determine molecular parameters by viscometry, light scattering or Size Exclusion Chromatography (SEC) it is a prerequisite to obtain molecularly dispersed and stable solutions.

Unfortunately, it has been reported that it is difficult to obtain molecularly dispersed solutions of PVA in water, besides these solutions may age [4–12]. Hence the solution properties change with time. These changes are attributed to the formation of aggregates a process depending on the thermal history of the polymer and the (dis)solution temperature [4,5]. This in turn leads to high values [7] for the Huggins constant (0.7 or even higher) in viscometry, to strongly curved angular dependencies [4,5], to extreme high molar masses as compared to the equivalent polyvinylacetate (PVAc) [6], to low or even negative second virial coefficients in light scattering. Often clogging of filters is also observed indicating the presence of gel or aggregates. The value for the exponent in the Mark–Houwink relation for PVA in water is relatively low at 25–30°C and only a minor scatter is observed in the literature: 0.62 [13,14], 0.63 [15] and 0.64 [16]. At higher temperature (80°C) a lesser value was observed (0.56 [5]). Hence the solvent quality decreases with increasing temperature. These findings indicate that water is only a moderate good solvent for PVA. The existence of the aggregates was also shown by Nagy [8] in the chromatograms of Size Exclusion Chromatography (SEC) coupled with Low Angle Laser Light Scattering (SEC–LALLS) and Multi Angle Laser Light Scattering (MALLS) [9]. The formation of aggregates also causes a shear dependence of the viscosity of more concentrated solutions of PVA in water [10]. The ageing process can be suppressed by the addition of propanol [11] but not stopped

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Table 1
Synthesis route and M_w of various polyvinylalcohols used in this investigation

PVA	M_w (kg/mol)	Synthesis route
PVA1	15	Solution
PVA2	86	Solution
PVA3	69	Solution
PVA4	115	Bulk
PVA5	145	Bulk
PVA6	230	Bulk
PVA7	285	Bulk
PVA8	370	Bulk
PVA9	610	UV Bulk
PVA10	690	UV Bulk

[6,12]. To cope with these difficulties, it was proposed to modify PVA to PVAc [6]. Subsequent characterization of the PVAc should give the molecular structure of the PVA. However chemical modification [15] is not always as complete as desired and the procedure is time consuming. Finally, the modification with a workingup procedure might lead to partial fractionation and consequently to an over-estimation of the M_n.

In order to avoid the drawback of chemical modification and formation of aggregates an organic solvent should be applied. Haas and Makas [17] used triethylenediamine as a solvent for PVA. However degradation could not be prevented and this solvent is very poisonous. Hence application was not taken into account. Some investigators reported that DMSO is a better solvent for PVA [10,18] than water although no evidence has been given that PVA is molecularly dissolved. Tacx et al. [19,20] applied DMSO successfully as a solvent for PVA in SEC to determine the molar mass distribution of PVA. Based on these findings, we started an investigation aimed at a comparison of the dissolution behavior and the solution properties of PVA in the solvents: DMSO, ethyleneglycol and water.

2. Experimental

2.1. Preparation of PVA

Bulk and solution polymerization were employed for vinyl acetate according to the radical chain reaction (see Table 1).

2.1.1. Bulk polymerization

Distilled vinyl acetate (500 g) was placed in a 1000 ml 3-necked flask, fitted with a condenser, a thermometer, and a gas dispersion tube. Nitrogen was introduced by bubbling through the solution for 2 h in order to remove air from the system.

At the same time the initiator was dissolved in vinyl acetate and made oxygen free. The monomer solution was heated up to 40°C and the initiator solution (Perkadox 16) was added slowly with a pump. The temperature was kept at 40°C. After 3.5 h when the polymerization temperature increases, the polymerization was stopped by adding hydrochinon.

The unreacted monomer was evaporated under vacuum at 50°C.

2.1.2. Solution polymerization

Methanol and vinylacetate (50/50 (wt/wt)) were placed in a reactor fitted with a thermometer, a condenser and a nitrogen inlet. The solution was heated up to 60°C and the initiator (Perkadox 16) was added. The temperature was kept at 60°C. After 0.5 h the polymerization was stopped by adding hydrochinon. Methanol and unreacted monomer were evaporated under vacuum at 50°C.

2.1.3. UV bulk polymerization

Destilled vinyl acetate (900 g) was placed in a glass reactor fitted with a thermometer and a nitrogen inlet. A high pressure ultra violet lamp (Heraeus, TQ 150) was placed outside the flask about 75 mm from the reactor [21].

The monomer was purified by three cycles of a degassing process. A solution of 13 mg AIBN in 100 g purified vinylacetate was added to the monomer. The solution was cooled to −35°C and irradiated with ultra violet light over a period of 52 h. At the end of polymerization hydrochinon was added. The solution was heated to room temperature. The unreacted monomer was distilled from the mixture at 50°C under vacuum.

These polymerization conditions were chosen to prevent the formation of long chain branching (LCB). The characteristics of the samples are mentioned in Table 2.

Table 2
Characteristics of the PVA used in this investigation

PVA	M_w (kg/mol)	A_2 (cm^3 gr^{-2} mol)	$[\eta]_{DMSO}$ (dl/g)	$[\eta]_{EG}$ (dl/g)	$[\eta]_{Water}$ (dl/g)
PVA3	69	8	1.24	0.79	0.73
PVA5	145	8	1.97	1.18	1.04
PVA6	230	12	2.98	1.84	1.50
PVA7	285	15	4.24	2.28	1.92
PVA8	370	12	4.86	2.51	2.15
PVA9	610	4	6.65	3.10	2.63
PVA10	690	9	7.55	4.08	3.05

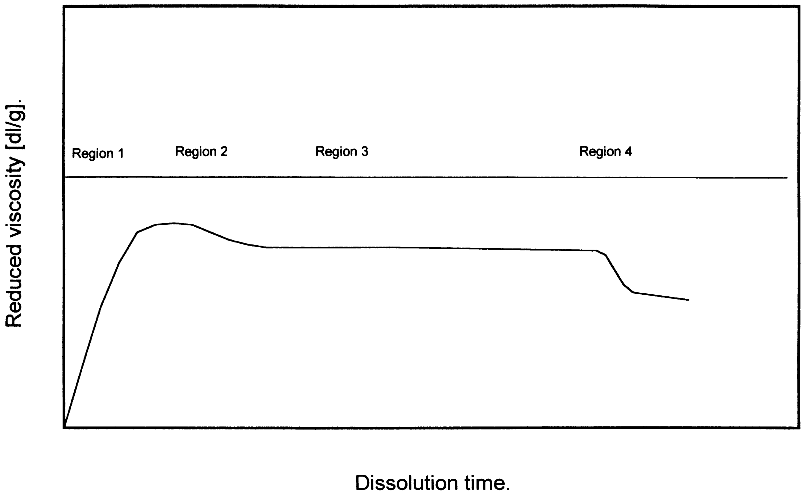

Fig. 1. Schematic representation of a dissolution/degradation curve.

Saponification of the polymers was carried out using the method of Beresniewicz [15]. All the polymers were saponified for at least 99.6% as determined by ^{1}H NMR.

2.2. Characterization of PVA

2.2.1. Dissolution of PVA

The PVA powders were dissolved in water (Milli-Q, Waters, MA, USA) by heating at 98°C for 4 h and shaking during cooling till 30°C [14]. Two grades of DMSO were applied: spectrophotometric grade and synthesis grade. Unless indicated the spectrophotometric grade was applied. In DMSO (Merck, spectrophotometric grade) the PVA powders were dissolved at 65°C for 11 h and the yarns were dissolved at 120°C for 4 h. When ethyleneglycol (Merck, pa) was used, the polymers were dissolved for 4 h at 140°C. The solvents were used as supplied.

2.2.2. Viscometry

Intrinsic viscometry measurements were carried out using an Ubbelohde capillary viscometer having an internal diameter of 0.5 mm and a length of 15 cm. The flow times were measured by using a viscotimer (Lauda). Corrections for kinetic energy could be ignored as the flow times ($t_0 > 100$ s) were relatively long. The polymers were dissolved in the viscometer reservoir and the solutions were subsequently diluted by adding fresh solvent. The solutions were stirred gently by a magnetic stirrer.

2.2.3. Light scattering

Light scattering experiments were carried out by using a SOFICA FICA 50 apparatus. The intensity of scattered light was measured at four different concentrations and 11 angles ranging from 30 to 150°. The equipment was calibrated using benzene. The solutions of PVA in DMSO were prepared at 65°C using the aforementioned procedure and subsequently quenched to 25°C. The solutions of reacetylated PVAc in dichloromethane were made at 25°C by dissolving the polymer for 4 h. The solvent and the solutions were filtered using 1.2 μ Millipore filters.

2.2.4. Differential refractometry

The specific refractive index increment was determined using a Brice–Phoenix differential refractometer operating at 25°C. The apparatus was calibrated according to the well known procedure [22] using potassium chloride.

3. Results

3.1. Dissolution behavior of PVA

Measuring the flow times of a very dilute solution of a polymer in an Ubbelohde viscometer is an excellent method to gain insight into the time required for a polymer to dissolve and the stability of the solution obtained. A so-called dissolution/degradation curve can be obtained.

First, the flow time of the solvent (blanc, t_0) is determined. Subsequently, the polymer sample is added to the solvent, which is stirred continuously, and finally η_{sp}/c is measured as a function of time. Generally, the dissolution/degradation curve can be divided into four characteristic regions as indicated in Fig. 1. At first (region 1) an increasing value of η_{sp}/c as a function of time is observed, because the polymer dissolves. After passing through a maximum value, η_{sp}/c decreases (region 2) until a constant level is reached. This decrease might be caused by dissolution of entangled molecules. Region 3 is characterized by a constant level of η_{sp}/c. In region 4 a further decrease of η_{sp}/c is observed which must be attributed to chain scission caused by oxidation or hydrolysis.

In Figs. 2 and 3 the dissolution/degradation curves, respectively in DMSO (synthesis grade) are presented of PVA1, 2 and 4 having molar masses of 15, 86 and

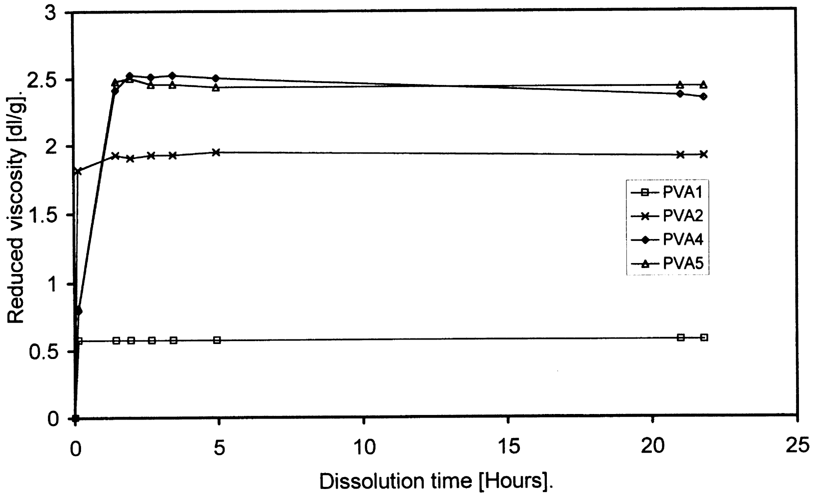

Fig. 2. Dissolution/degradation curves of PVA1, 2, 4 and 5 in DMSO (synthesis grade) at 60°C. Concentrations are 0.25 g/dl.

115 kg/mol determined at 60 and 80°C. From these results it is concluded that the polymers dissolve reasonably fast within 3 h and that the solutions do not show a characteristic region 2. This is attributed to the relatively low molar masses. The dissolution time increases as expected with increasing molar mass. However PVA4 with a molar mass of 115 kg/mol shows significant degradation which becomes detrimental at 100°C (Fig. 4). From this result it is clear that the expected maximum value is not reached. Fortunately, application of spectrophotometric DMSO grade shows a significant improvement of the solution stability. The dissolution/degradation curves of PVA6, 8 and 10 in DMSO (spectrophotometric grade) at 65°C are presented in Fig. 5. It appears that the dissolution time increases from 3 to 11 h when the molar mass increases from 115 to 690 kg/mol. At the highest molar mass the dissolution time is dependent on concentration. Decreasing the concentration from 0.1 to 0.05 g/dl, the dissolution time decreases from 11 to 5 h. In Fig. 6 the dissolution/degradation curves at 110°C of the same polymers is presented. The dissolution time of PVA10 (having the highest molar mass) at 0.1 g/dl decreases from 11 to 3 h for a temperature rise from 65 to 110°C. It should be emphasized that even the polymers having very high molar masses show only minor degradation. At 110°C a decrease of 4 and 7.5% is observed after 8 and 19 h, respectively. Based on these findings, the DMSO (spectrophotometric grade) was applied throughout.

The same samples were also dissolved in ethyleneglycol at 140°C. This temperature was considered to be the upper limit. Application of higher temperatures was not taken into account because of limitations in the SEC apparatus. Fig. 7 shows that also at these temperatures stable dilute solutions can be obtained for at least 24 h.

The dissolution/degradation curves of PVA1, 2, 4 in water and in water with sodium nitrate at 80°C are given

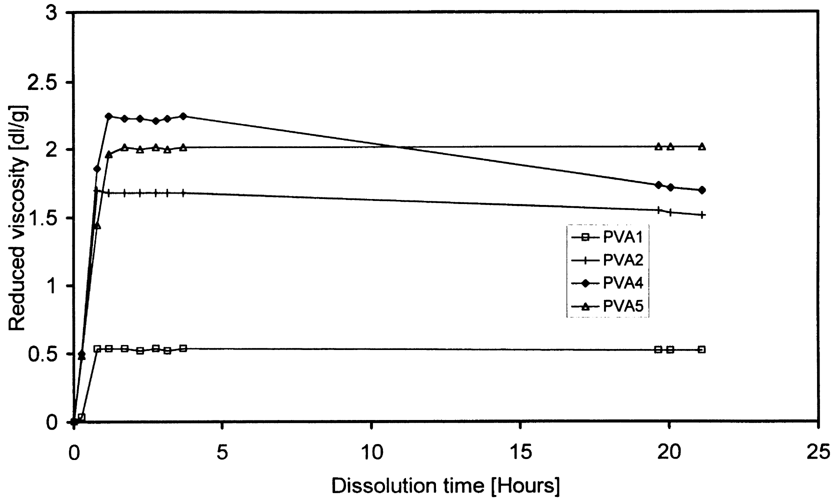

Fig. 3. Dissolution/degradation curves of PVA1, 2, 4 and 5 in DMSO (synthesis grade) at 80°C. Concentrations applied are 0.25 g/dl.

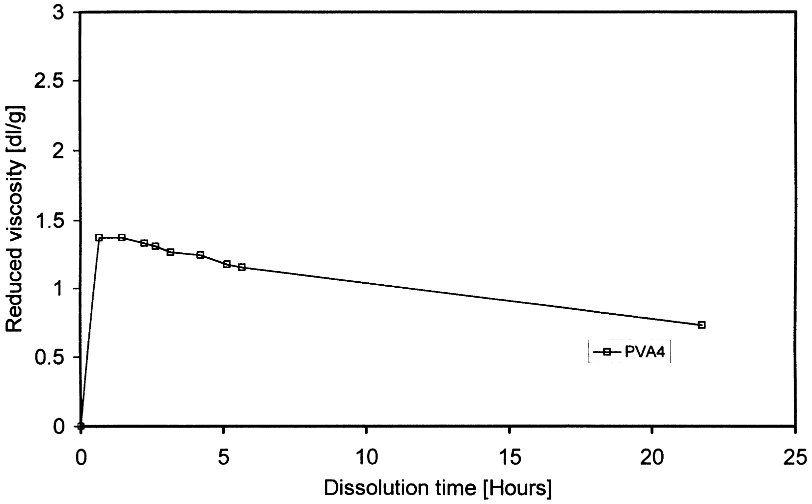

Fig. 4. Dissolution/degradation curves of PVA4 ($c = 0.25$ g/dl) in DMSO (synthesis grade) at 110°C.

in Fig. 8. It appears that the polymer dissolves within 4 h and that the solution remains stable for at least 120 h.

In a later stage of the investigation, yarns were prepared using the well-known gel-spinning route [24]. The dissolution/degradation curves of the yarn from 90 till 120°C are presented in Fig. 9. It becomes clear that the yarn does not dissolve in DMSO at 90°C; at 95°C the dissolution time is still 20 h but at 110°C the polymer dissolves within 3 h and at 120°C it dissolves in 2 h. The yarn appeared to be insoluble in water at temperatures ranging from 60 to 100°C. This behavior must be explained by an increase of the orientation of the amorphous phase or the degree of crystallinity. Reduction of the crystallinity can be an efficient method to dissolve the polymer. This procedure was also successfully applied by Schoffeleers et al. [23] to dissolve liquid crystalline polymers (LCPs). Unfortunately, this approach was not successful for PVA as degradation occurred before complete melting of the polymer. This caused anomalous solution behavior. Ethyleneglycol was not applied for the yarn.

Based on these findings it was concluded that PVA with molar masses ranging from 15 to 690 kg/mol could successfully be dissolved in DMSO within 11 h at 65°C and 3 h at 110°C. Moreover stable solutions are obtained for at least 24 h even at 120°C.

3.2. Light scattering

The polymers of Table 2 were characterized using light scattering. The molar masses range from 65 to 690 kg/mol and the second virial coefficient from 4 to 15×10^{-4} cm^3 g^{-2} mol. It should be emphasized that these values for the second virial coefficient are high. The literature values for the second virial coefficient for PVA in water are typically 2×10^{-4} or even negative [4,5]. In Fig. 10, two Zimm plots are given for PVA5 and PVA9 in DMSO. It is

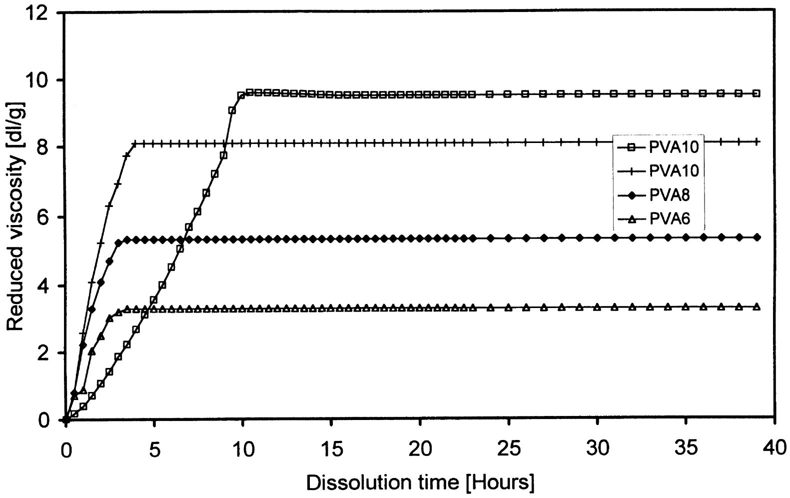

Fig. 5. Dissolution/degradation curves of PVA in DMSO (spectrophotometric grade) at 65°C. Concentrations applied are: □: PVA10 (0.1 g/dl), +: PVA10 (0.05 g/dl), PVA8 and PVA6 (0.1 g/dl).

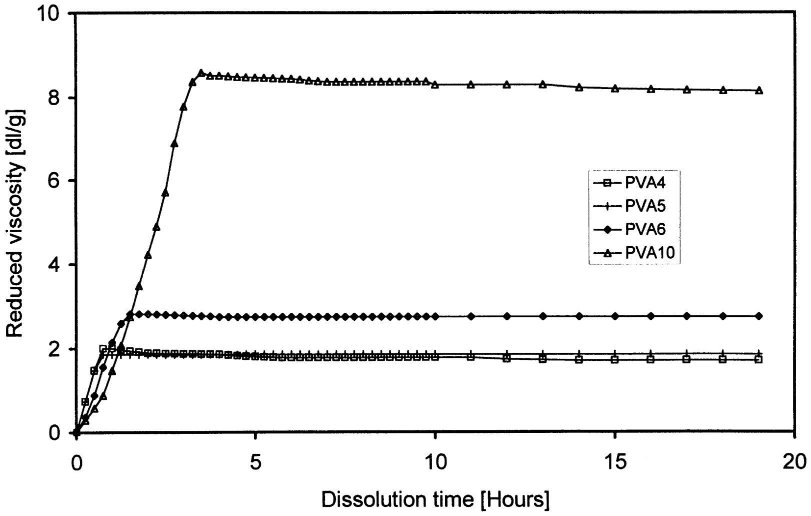

Fig. 6. Dissolution/degradation curves of PVA4 ($c = 0.160$ g/dl), 5 ($c = 0.16$ g/dl), 6 ($c = 0.11$ g/dl) and 10 ($c = 0.10$ g/dl) in DMSO (spectrophotometric grade) at 110°C.

seen that an approximately straight angular dependence is obtained even up to the lowest angle of measurement i.e. 30°. This might indicate the absence of aggregates. Moreover the Zimm plots for PVA5 appeared to be easily reproducible (values for $M_w = 140$, 150 kg/mol, respectively). The same polymer was also dissolved for only 2 h at 65°C. From the dissolution/degradation curves it is clear that the polymer is not dissolved completely. In Fig. 11 the light scattering results for this experiment are presented. A stronger angular dependence is observed indicating the presence of aggregates. Moreover the molar mass obtained (400 kg/mol) is far too high and the second virial coefficient is too low in comparison to the experiments in which the polymer is molecularly dissolved. A solution of PVA was kept at 25°C for 5 days. After this period, the angular dependence of the scattered intensity was measured again. Fortunately, no increase in intensity was observed indicating that no additional aggregation occurred. Hence it might be concluded that the solutions are stable and do not aggregate.

As an important result we found that PVA8 solutions in DMSO caused no increase in pressure during the filtration process, even after applying a 0.2 μm filter. However a similar water solution of PVA8 could not be filtered even when vacuum was applied. Decisive evidence for the state of dissolution is obtained by comparison of the molar mass obtained by characterization of PVA and that of the equivalent PVAc. In order to get evidence for this, PVA5 was carefully reacetylated using the earlier published method [6]. Subsequently, the sample was characterized using light scattering. The molar mass obtained for this polymer was 340 kg/mol which is equivalent to 170 kg/mol for the molar mass of PVA. Taking into account the errors of measurement, the data (145 and 170 kg/mol) agree

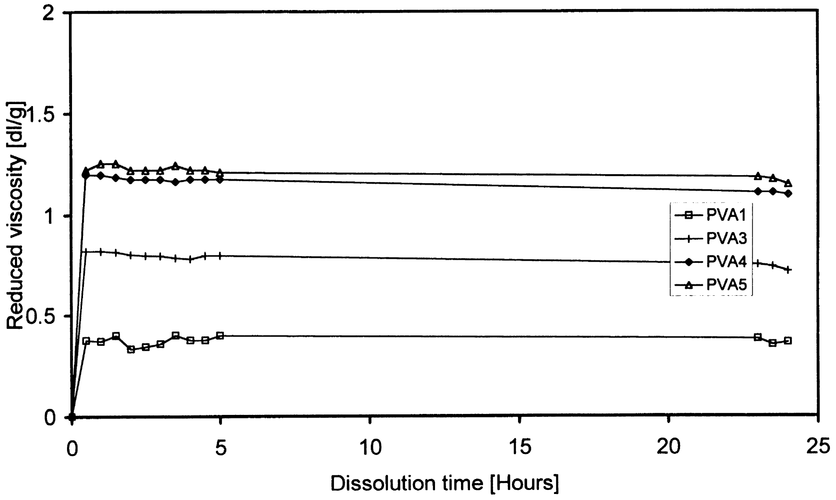

Fig. 7. Dissolution/degradation curves of PVA1, 3, 4 and 5 in ethyleneglycol at 140°C. Concentrations are 0.25 g/dl.

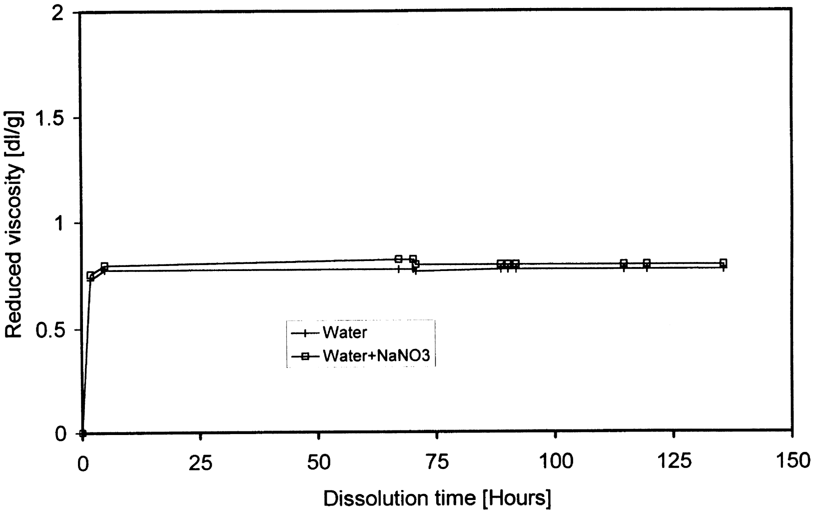

Fig. 8. Dissolution/degradation curves of PVA1 ($c = 0.25$ g/dl) in water at 80°C.

reasonably well. The results inevitably indicate that PVA forms molecularly dispersed solutions in DMSO and that the polymer solution does not show aggregation.

3.3. Mark–Houwink relations of PVA in DMSO, ethyleneglycol and water

The intrinsic viscosity of the polymers was determined in three solvents, DMSO, ethyleneglycol and water. The results are presented in Table 2. The Huggins constants of PVA in DMSO, ethyleneglycol and water are 0.3, 0.5 and 0.5–0.6, respectively. Clearly, the intrinsic viscosities increase significantly from water to ethyleneglycol and DMSO, in agreement with the results of Schurz [10]. He found that the ratio of the intrinsic viscosities of PVA in DMSO and water increased with increasing molar mass, indicating that the exponent in the Mark–Houwink relation must be greater for PVA in DMSO than in water.

The intrinsic viscosity is proportional to the mass average molar mass according to the Mark–Houwink relation of Eq. (1):

$$[\eta] = KM_{\mathrm{w}}^{a}. \tag{1}$$

In our investigation no attempt was made to correct the difference between M_{v} and M_{w}. This can be carried out by taking into account a relation between the two moments of the distribution. For a log normal distribution a well known relation can be derived [25,26]. Although the polydispersities determined according to Tacx [19] ranged from 2.3 to 3.4, correction was considered to be of limited value as the distributions do not show a log normal shape. Hence the correction introduces an unknown error. The Mark–Houwink relations are presented in Fig. 12. The Mark–Houwink relations for PVA in the various solvents were calculated using Eq. (1) and the data given in Table 2.

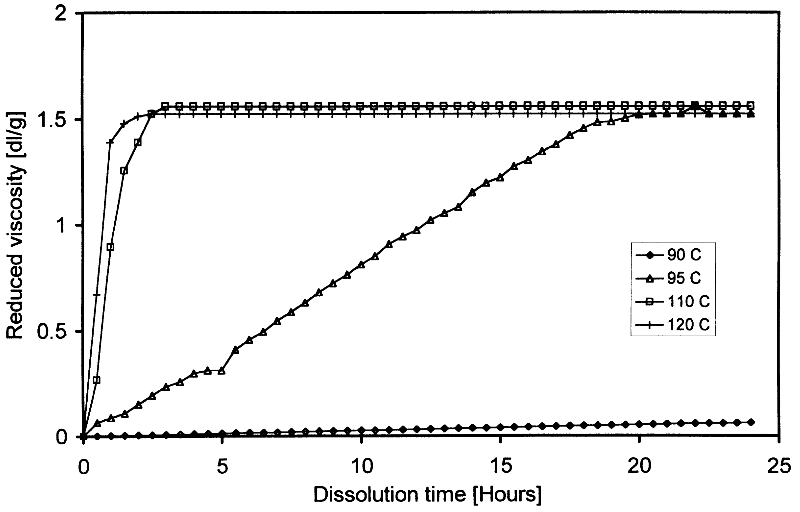

Fig. 9. Dissolution/degradation curves of PVA yarn in DMSO (spectrophotometric grade) at 90, 95, 110 and 120°C.

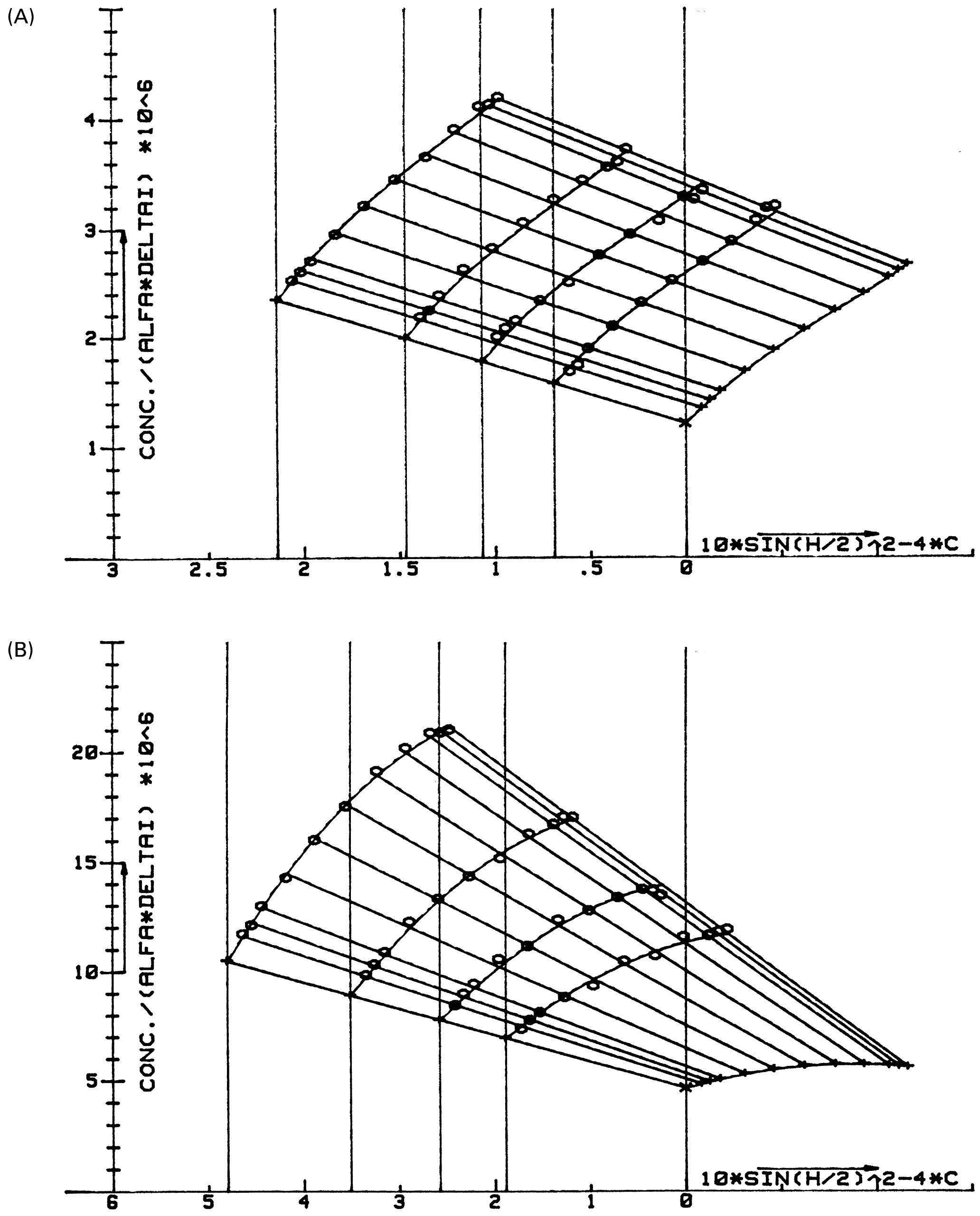

Fig. 10. Zimm-plots of PVA9 (A) and PVA5 (B) in DMSO (spectrophotometric grade).

The following results were obtained ($69 < M_w < 690$ kg/mol):

PVA in DMSO at 65°C:
$[\eta] = 1.51 \times 10^{-4} M_w^{0.804}$
PVA in ethyleneglycol at 140°C:
$[\eta] = 3.54 \times 10^{-4} M_w^{0.692}$
PVA in water at 30°C:
$[\eta] = 6.51 \times 10^{-4} M_w^{0.628}$

The relations obtained for water are in agreement with the relations mentioned by Elias [13] and the Japanese industrial standard (JIS) [14]. The results inevitably indicate that DMSO is the best solvent for PVA. Moreover a straight Mark–Houwink relation and a high value for the exponent indicates the absence of LCB in the PVA.

3.4. Anomalous behavior of PVA in water–DMSO mixtures

Mixtures of DMSO and water at 30°C exhibit an apparent anomalous viscosity behavior (Fig. 13). Diluting DMSO, the flow times and hence the viscosity increases significantly. This behavior was not expected on grounds of the simple additivity rule as the flow time of water at this experimental setup is very low compared to that of DMSO. A maximum is reached at 30 wt.% water (Fig. 14). Subsequently, the flow times decrease continuously with

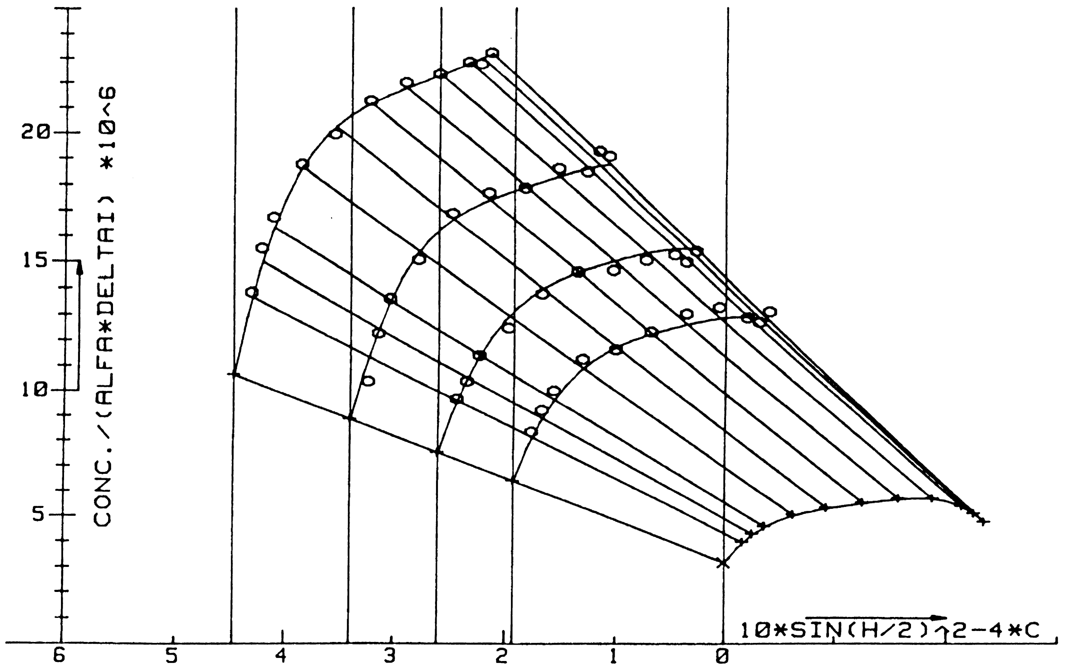

Fig. 11. Zimm-plots of PVA5 dissolved incompletely.

increasing water content. This behavior must be explained by the strong interaction between water and DMSO resulting in the complex formation of and hence an apparent increase of the molar size. The formation of heat on mixing water and DMSO is also a result of the strong interaction. The intrinsic viscosity of PVA5 was determined at various compositions of the DMSO–water mixtures. Also in this case the intrinsic viscosity which decreases for higher water content, cannot be described by a simple additivity model. The intrinsic viscosity decreases with increasing water content. However exceeding by some 70 wt.% of water, the intrinsic viscosity can be predicted by additivity.

Vercauteren et al. [6,27] presented a tentative model to explain the aggregation of the PVA in water. Water forms hydrogen bonds between two polymer chains. At low temperatures (30°C) there is a reasonably good interaction between PVA and water. Acting much like a zipper, water brings chains together, resulting in the formation of aggregates. At high temperatures (>95°C) there is a moderate interaction between water and PVA resulting in the disappearance of the zipper action. At these temperatures the amorphous regions break up. Based on our findings we assume that DMSO strongly interacts with PVA and also forms hydrogen bonds but only with one chain. As a consequence, DMSO cannot act like a zipper and the PVA molecules cannot reach each other. This might explain the

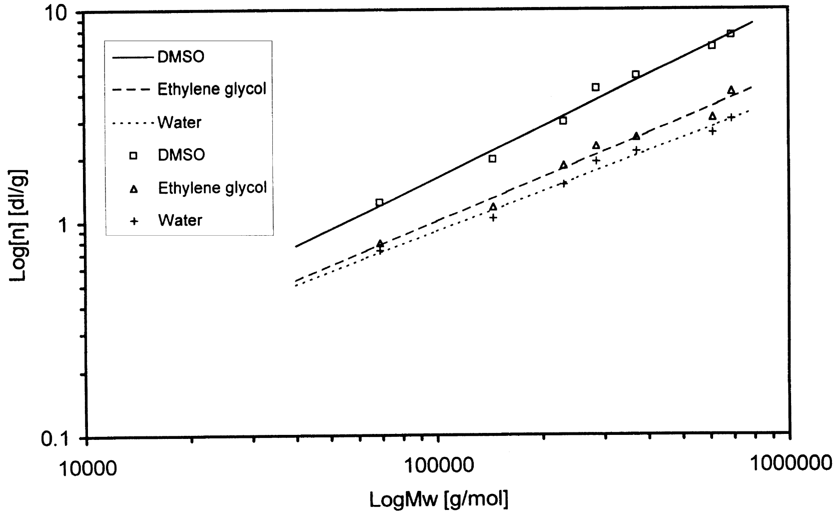

Fig. 12. Mark–Houwink relations of PVA in DMSO (65°C), ethyleneglycol (140°C) and water (30°C).

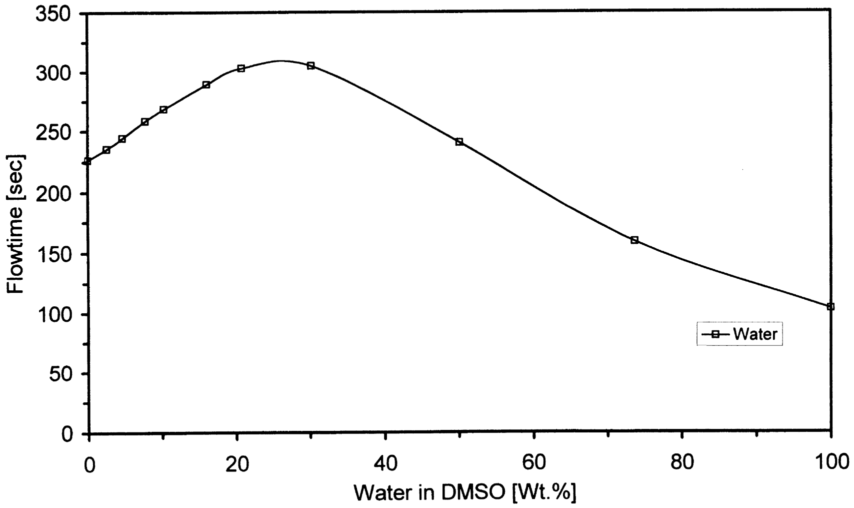

Fig. 13. Flow time (seconds) of DMSO–water mixtures as a function of the water content (wt.%) at 30°C.

difference between the two solvents for PVA. However if the two solvents are mixed, a strong interaction exists between the two low molar mass components resulting in a decrease of the interaction with PVA. Hence the intrinsic viscosity decreases with increasing dilution of DMSO.

4. Conclusions

The solvent quality of water, ethyleneglycol and DMSO towards PVA increases strongly in this order. This conclusion is based on the increasing values for the intrinsic viscosity, the decreasing Huggins constant of the increasing second virial coefficient and exponent in the Mark–Houwink relation. Saponified atactic PVA with molar masses ranging from 15 to 690 kg/mol dissolve readily within 11 h at 65°C and 3 h at 110°C. The solutions obtained were stable for at least 24 h even at 120°C. Only PVA with the highest molar mass i.e. 690 kg/mol, a minor degradation of approximately 7.5% was shown after 19 h at 110°C. Even yarns which are virtually insoluble in water, could successfully be dissolved in DMSO at 120°C. From light scattering experiments on PVA and reacetylated PVA, it could be concluded that PVA is molecularly dissolved in DMSO and that the solutions do not age. The Mark–Houwink relations for PVA in DMSO, ethyleneglycol and water were established.

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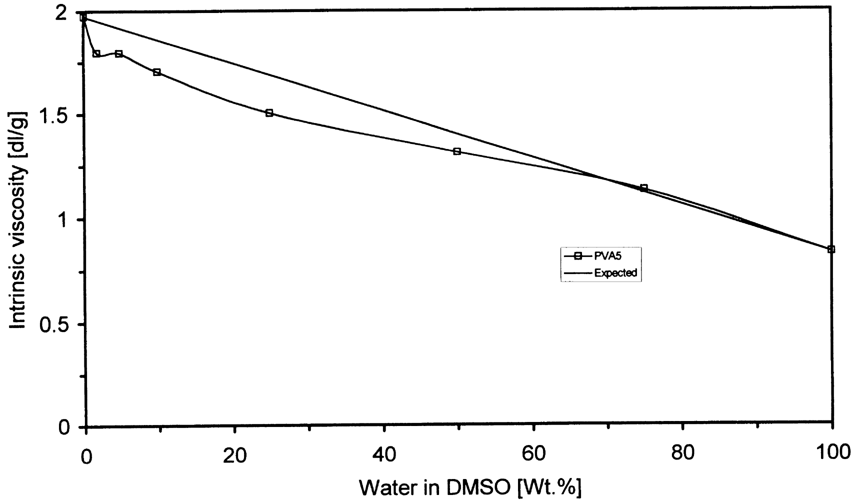

Fig. 14. Dependence of the intrinsic viscosity (IV) (dl/g) of PVA5 on the water content in the solvent (DMSO–water mixture) at 30°C.

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