Influence of the molecular structure of poly(vinyl alcohol) on the ultrasonic absorption

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The properties of poly(vinyl alcohol) are essentially determined by the content of residual acetate groups. In this paper the influence of the molecular structure on the ultrasonic absorption is studied. As structure parameters, the residual acetate content and the ^{13}C n.m.r. microstructure parameters are determined. Some commercial and laboratory products prepared by different methods are investigated. Broad ultrasonic absorption spectra are obtained. The theory of normal mode relaxation of the Rouse–Zimm type can be applied. For products with higher acetate contents, notable discrepancies between normal mode losses and measured absorption occur. The influence of acetate content and block structure on ultrasonic absorption is demonstrated but the absorption behaviour cannot only be explained by both parameters in all cases.

INTRODUCTION

The investigation of properties of poly(vinyl alcohol)–water solutions is problematic. In previous papers it has been reported that ultrasonic methods yield information about the intra- and intermolecular structure[1-3], for example, about the phenomenon of gelation[5]. Pethrick *et al.*[4] have reported on ultrasonic studies of aqueous solutions of poly(vinyl alcohol). The study has allowed the identification of polymer–polymer and polymer–solvent interaction. The aim of this work is to investigate the relation between molecular structure and ultrasonic absorption of concentrated poly(vinyl alcohol) solutions. Mainly commercial products and some laboratory products are investigated. Poly(vinyl alcohol) (PVA) is obtained by the saponification of poly(vinyl acetate) (PVAC). Generally, this saponification is not complete and as a consequence PVA will contain a significant quantity of residual acetate groups. Usually it is distinguished between fully hydrolysed (degree of hydrolysis 97–100%) and partly hydrolysed (degre of hydrolysis 80–90%) products[6]. The residual acetate content essentially determines the application properties of PVA. Both the brutto content of VAC and the sequence length distribution can be considered as structural parameters[7,8]. The PVA samples are well characterized by mean molecular weight, contents of residual acetate groups and sequence length parameters determined by ^{13}C n.m.r. measurements.

EXPERIMENTAL

Materials

Several unfractionated commercial products of PVA having different molecular weights and residual acetate contents were used in this study. Further, samples have been prepared with different contents of acetate groups by several methods. The characteristic data of the samples investigated are summarized in *Table 1*. The mean molecular weight $\bar{M}$ was determined by intrinsic viscosity measurements using the interpretation by Beresniewiecz[12].

The VAC contents x_{VAC} were deduced by both full saponification and from n.m.r. analysis.

The remaining seven samples were prepared in the laboratory by different methods:

(1) alcoholysis of PVAC LE 60/40 (Buna)—P 10, P 11, P 12.

(2) homogeneous re-acetylation of PVAL 55/02 (Buna)—R 1, R 2.

(3) heterogenous re-acetylation of PVAL 55/02, swollen in pyridine—B 1, B 2.

Methods

The ultrasonic absorption measurements were carried out using the following methods: (1) statistical reverberation in the frequency range (0.5–3 MHz) using polyethylene bulbs as the measuring cells[5]; (2) a differential method (2–25 MHz)[10]; and (3) a pulse method using the variable transducer distance (25–150 MHz)[11].

The ^{13}C n.m.r. spectra were recorded on a Bruker-FT-n.m.r. spectrometer HX-90 R.

The ^{13}C n.m.r. spectrum of partly hydrolysed PVA is shown in *Figure 1*. The methylene resonances used in the sequence analysis are separated into three. They can be associated with the following triads:

(1) CHOH–CH$_2$–CHOH　　　(AA)

Table 1 PVA materials

	Probes	x_{VAC} (%)	$\bar{M} \cdot 10^{-3}$	$\bar{l}_{VA}$	$\bar{l}_{VAC}$	r
P 1	PVAL 55/02	1.6	86	20.1	2.9	0.39
P 2	Gohsenol KH 17	16.7	290	10.0	2.5	0.50
P 3	Gohsenol KH 20	16.5	398	11.7	2.7	0.45
P 4	Gohsenol KP 08	21.3	112	9.7	2.6	0.48
P 5	Polyviol W 25/240	16.8		9.0	2.7	0.48
P 6	Polyviol W 40/140	10.8	242	16.4	2.8	0.42
P 7	Poval 420	15.8	281	8.5	2.7	0.49
P 8	Alkotex 75 L	21.5	89	8.3	2.9	0.46
P 9	PVAL 65/15	10.5	140	19.0	3.0	0.39
P 10		1.0				
P 11		11.4				
P 12		16.4				
R 1		25.0		4.4	1.7	0.83
R 2		3.0		–	–	–
B 1		17.0		10.8	2.1	0.56
B 2		23.0		7.5	2.5	0.53
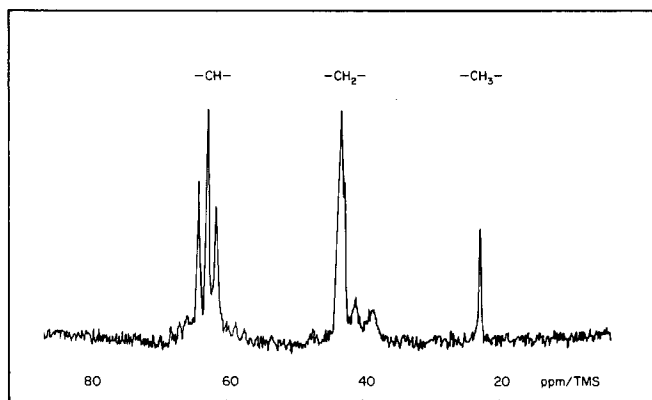
Figure 1 ^{13}C n.m.r. spectrum of partly hydrolysed PVA (x_{VAC}: 12%; $r=0.47$)

(2) CHOAc–CH$_2$–CHOH   (AB)

(3) CHOAc–CH$_2$–CHOAc   (BB)
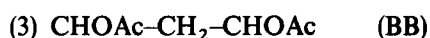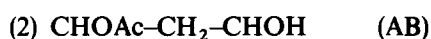
The areas under the lines (F_{AA}, F_{AB}, F_{BB}) are equivalent to the contents of these units.

The probabilities of (P_{AA}, P_{AB}, P_{BB}) for the existence of the the triads can be calculated according to equation (1):

$$P_{AA} = \frac{F_{AA}}{F_{AA} + F_{AB} + F_{BB}}$$

$$P_{AB} = \frac{F_{AB}}{F_{AA} + F_{AB} + F_{BB}} \qquad (1)$$

$$P_{BB} = \frac{F_{BB}}{F_{AA} + F_{AB} + F_{BB}}$$

The mean sequence lengths T_A and T_B can be calculated by the following equations:

$$\bar{l}_A = \frac{2P_{AA}}{P_{AA}} + 1$$

$$\qquad (2)$$

$$\bar{l}_B = \frac{2P_{BB}}{P_{AB}} + 1$$

The block character is expressed in terms of the block number R (R_S for statistical distribution):

$$R = 100P_{AB}$$

or the block parameter:

$$r = R/R_s \qquad (3)$$

Ultrasonic absorption in concentrated polymer solutions

The relaxation absorption in polymer solutions has been explained by different models: (1) the normal mode model[13-15]; and (2) the local mode model[16-18].

The whole topic of the analysis of high frequency motions has been reviewed[25,26]. In numerous papers North *et al.*[21-24] have discussed and analysed the contribution of normal modes and local motions to the ultrasonic attenuation in different polymer solutions.

The results here on concentrated PVA–water solutions indicate that the application of the theory of normal mode relaxation of the Rouse–Zimm-type is useful. If additional thermal losses do not exist then the ultrasonic absorption can be calculated in terms of the following expression:

$$\frac{\Delta\alpha}{f^2} = \frac{2\pi^2}{\varphi v^3}(\tfrac{4}{3}\eta_s' + \eta_v') \qquad (4)$$

where η_v', the volume viscosity, is in the same order as the shear viscosity, i.e. $\eta_v'/\eta_s' \approx 1$. v is the ultrasonic velocity, f the frequency and $\Delta\alpha$ the excess absorption. According to the theory of Rouse[13] the dynamic viscosity is:

$$\eta_s' = nkT \sum_{p=1}^{N} \frac{\tau_p}{1 + (\omega\tau_p)^2} \qquad (5)$$

with

$$\tau_p = 6(\eta_0 - \eta_1)M/\pi^2 \cdot p^2 cRT \qquad (6)$$

η_1 is the viscosity of the solvent, η_0 the steady shear viscosity of the solution, τ_p the relaxation time of the pth mode, M the molecular weight and T the temperature. Onogi *et al.*[19] have shown that this theory is applicable to concentrated PVA solutions within an accuracy of one order.

RESULTS AND DISCUSSION

^{13}C n.m.r. analysis

Some selected microstructure parameters of sequence length analysis are given in *Table 1*. The data indicate a slight block structure in all of the industrial products

examined. A mean block parameter $r=0.47\pm0.06$ was determined for the commercial PVA products. The homogeneous re-acetylated products tend towards a more statistical distribution whereas the heterogeneous re-acetylated samples exhibit a block structure.

Ultrasonic absorption

Ultrasonic absorption spectra of PVA–water solutions are shown in *Figure 2*. Within the experimental error the results were fitted by straight lines. The absorption amplitudes are very different in the low frequency range.

The following classification is proposed:

(1) slope 0.4–0.5
    samples P 1, P 2, P 3, P 5, P 6, P 9, P 11

For this group the model of normal mode relaxation of Rouse–Zimm type can be successfully applied. The slope <0.5 represents the non-free draining case corresponding to the theory of Zimm[14].

(2) slope >0.5:
    samples P 7 $n=0.62$; P 4 $n=0.74$;
             P 8 $n=0.78$

A slope >0.5 could be related to gelation[7]. The viscosity measurements do not show these effects, but influences of microgels or molecular aggregates on the ultrasonic absorption cannot be completely excluded. However, the notable discrepancy between the normal mode part of the absorption and the measured absorption is attributed to additional losses which must be related to the compressional stress of the longitudinal wave or to thermal relaxation processes.

Table 2 shows the ratio η'_v/η'_s for different frequencies. The plot of the reduced dynamic viscosity *versus* frequency (*Figure 3*) shows a good correlation between the steady shear viscosity and the ultrasonic absorption values in the samples with $n=0.4$–0.5 whereas in the samples with $n>0.5$ a notable discrepancy between the normal mode portion and measured absorption occurs.
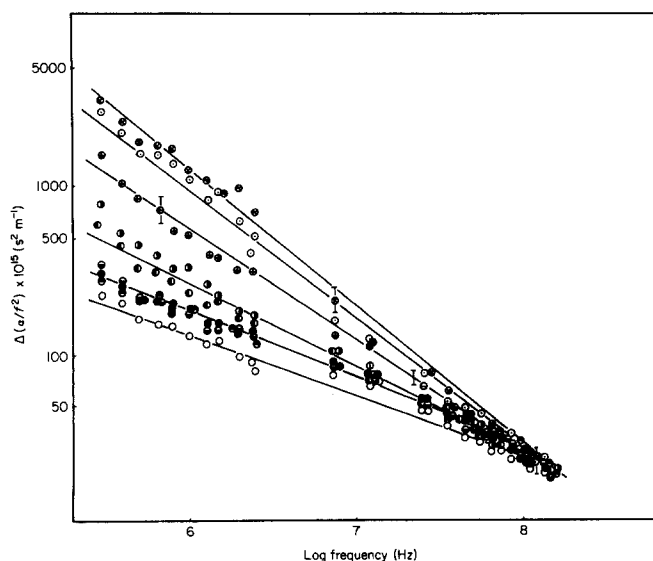
Using the normal mode theory of Rouse qualitatively identical statements are obtained (*Table 3*).

The absorption spectra of the laboratory products are presented in *Figures 4* and *5*. The samples P 10–P 12, obtained by alcoholysis, differ only in the residual acetate contents. The influence of the overall composition on ultrasonic absorption is evident. The probes R1, R2, B1, B2 differ both in VAC content and sequence length distribution. It is observed that the ultrasonic absorption depends additionally on block structure. With increasing blockiness the ultrasonic absorption increases also (samples R1, B2).

CONCLUSIONS

The investigations of the laboratory products indicate the influence of the residual acetate content and the structural variation on the ultrasonic absorption.

The relaxation behaviour of all samples examined is typical of relaxation time distributions. Differences of the absolute absorption of the samples occur only in the low frequency range. For the fully hydrolysed products, the theory of normal mode relaxation of Rouse–Zimm type is generally applicable, whereas in partly hydrolysed pro-

Table 2 The frequency dependence of the ratio η'_v/η'_s for PVA samples with deviations from the Rouse normal mode spectrum

	Frequency (MHz)						
	1	1.4	7.2	12	25	55	85
P 4	11.2	7.5	2.4	1.6	1.0	0.97	0.75
P 8	13.6	12.4	2.4	1.6	0.86	0.97	0.86

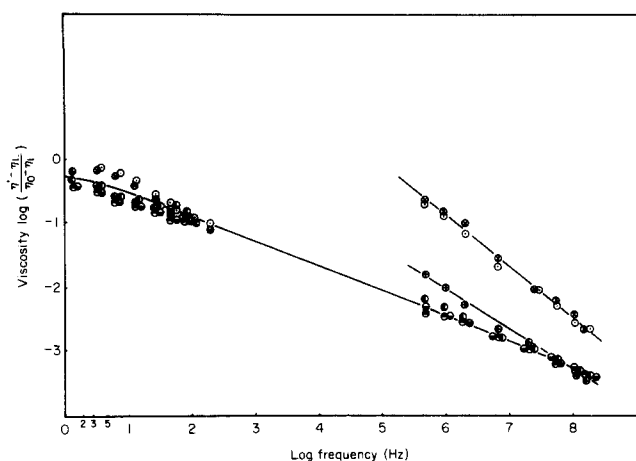**Figure 3** Reduced dynamical viscosity of PVA–water solutions (100 g l^{-1}, 298 K) (subscript zero refers to $\omega \to 0$). Assumptions: $\eta'_v/\eta'_s = \frac{2}{3}$; shear rate, $\dot{\gamma} = 2\pi f$, $\eta'_i = \eta_i$)
Key as *Figure 2*

Table 3 Experimental values of ultrasonic absorption at 1 MHz for selected PVA–water solutions (100 g l^{-1}, 298 K) and theoretical values according to the Rouse theory using the zero shear viscosity

	$\Delta\alpha/f_2 \cdot 10^{15}$ calc. $(m^{-1}s^2)$	$\Delta\alpha/f_2 \cdot 10^{15}$ exp. $(m^{-1}s^2)$
P 8	160	1200
P 4	180	1040
P 3	280	320
P 6	300	240

Figure 2 Ultrasonic absorption spectra of PVA–water solutions (100 g l^{-1}, 298 K). ○, P1; ◑, P2; ◓, P3; ⊙, P4; ◔, P5; ◕, P6; ⊕, P7; ⊗, P8; ●, P11
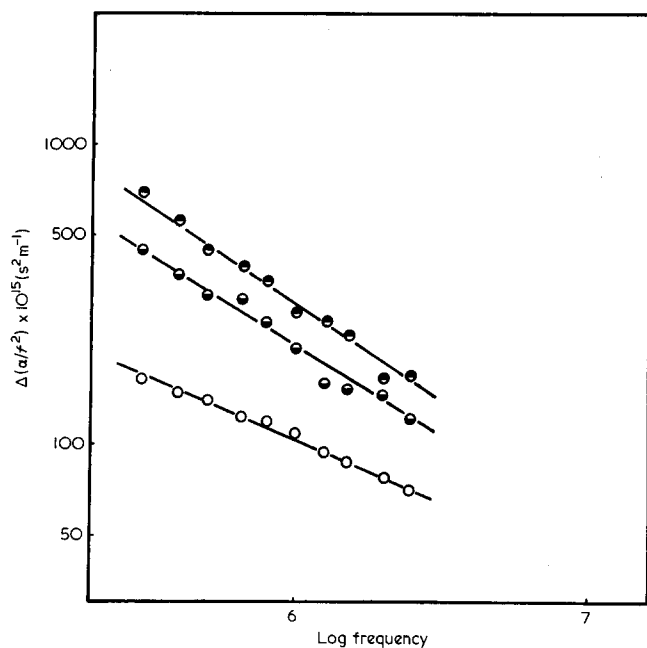
Figure 4 Ultrasonic absorption of PVA obtained by alcoholysis. (O, P10; ◐, P11; ◑, P12)
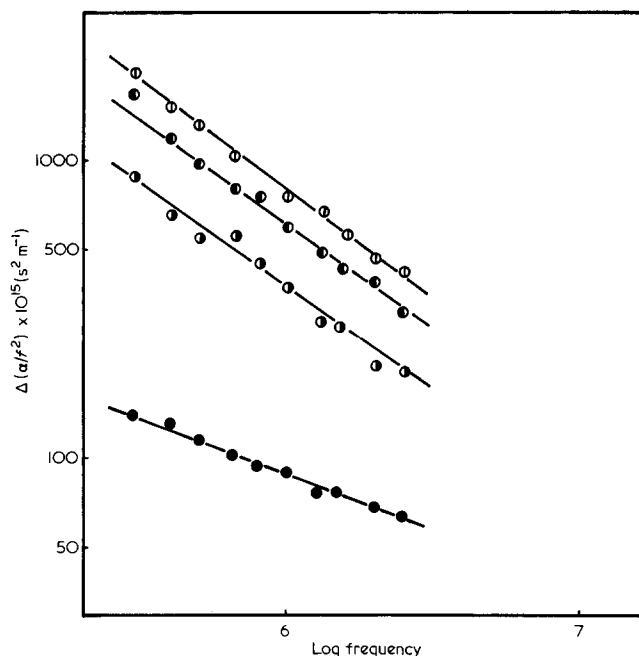

Figure 5 Ultrasonic absorption of PVA obtained by reacetylation. (◐, R1; ●, R2; ◑, B1; ◒, B22)

ducts with VAC-contents between 15 and 25 per cent the absorption spectra become increasingly similar to those of pure PVAC solvated in alcohol[20]. Therefore, it is assumed that the additional losses of partly hydrolysed PVA are attributed to thermal relaxation processes which are known to occur in pure PVAC solutions. In the case of (VA–VAC) copolymers they could be related to local motions within longer VAC sequences. In the case of the industrial samples the correlation between the ultrasonic absorption and the composition parameters determined by n.m.r. measurements is not very close. In fact, the n.m.r. microstructure parameters of all industrial products can be described in terms of the Bernoulli model with a mean block parameter $r = 0.47$ and significant differences in block structure could not be observed. However, it is known that the application properties of the investigated

samples (for instance the solubility or the colloid properties) are very different even for samples with nearly identical VAC content and mean molecular weight, respectively. This may be caused by differences of the intramolecular VAC distribution as well as of the molecular VAC content distribution. This chemical heterogeneity of partly hydrolysed PVA cannot be detected by the n.m.r. triad analysis. From this point of view it is noteworthy that the ultrasonic absorption spectra of the different PVA products show significant differences. The influence of VAC content is evident but the observed variations of the absorption spectra cannot be explained in terms of the structure parameters determined here.

Two reasons should be taken into consideration:

(1) The process which causes the differences in ultrasonic absorption is connected with longer VAC sequences. Therefore, it is necessary to know the real sequence length distribution.

(2) Possibly, additional structure parameters such as tacticity, the content of conjugated carbonyl structures or branching have to be taken into consideration.

The results show that the ultrasonic absorption is very sensitive to the molecular structure. Therefore, in future ultrasonic investigations of these solutions, it is evident that detailed characterization of the samples examined is necessary.

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