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Desaggregation

Desaggregation of Commercial Polyvinylbutyral in Dilute Solutions*

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Summary

Determination of the molecular parameters of commercial polyvinylbutyral in one-component organic solvents by the light scattering method is rather unreliable. It was found that the cause consists in a small quantity of aggregates, the formation of which can be avoided by dissolving the copolymer direct in a mixture of higher alcohols and water. We showed that from this viewpoint 2-propanol is the optimal choice, because polyvinylbutyral dissolves in it to the molecular form at a relatively broadest possible water content. The way of solvation of the copolymer chain in two-component solvents is demonstrated by means of total and preferential sorption.

Introduction

Commercial polyvinylbutyral (PVB) is a product of the simultaneous hydrolysis of poly(vinyl acetate) and of the acetalization of poly(vinyl alcohol) (PVA) thus formed with butyral aldehyde. As the polymeranalogous transformation is not complete, PVB is a copolymer which along with butyral rings also contains hydroxyl groups (usually, 10-20 wt.% PVA). These may become both donors and acceptors in the formation of intra- and intermolecular hydrogen bonds (1), which explains the considerable trend of PVB towards aggregation (2,3). These aggregates cannot be completely destroyed by any of the comparatively large number of simple organic solvents in which PVB can be visually dissolved. Even a small fraction of PVB which stays on in a dilute solution in the aggregated form may considerably distort determination of molecular parameters by light scattering which is one of the basic methods employed in the characterization of polymers.

It is known, however, that in the case of copolymers the addition of a nonsolvent which usually is a selective solvent for one of the copolymer components may improve considerably the "solvent power" of the original solvent, especially when the dissolution proceeds directly in the mixture (4-6).

We tried to use this procedure in solving problems connected with the aggregation of PVB in single solvents. We investigated the behaviour of this copolymer in a number of mixtures of organic solvents and water (solvent for PVA) with the aim of finding a suitable system for light scattering measurement.

Experimental

Polymer

We analyzed reprecipitated polydisperse commercial polyvinylbutyral (PVB)"Movital" Hoechst containing 70% monomer units of saponified poly(vinyl acetate) transformed into butyral. The remaining units are in the form of alcohol. Commercial PVB is assumed to be a statistical chemically homo-

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** To whom offprint requests should be sent geneous copolymer. The mass average relative molar mass of the sample used ($M_w = 2\times10^5$) was determined after acetalization (7), and also by the SEC analysis (8). The number average molar mass ($M_n = 1.05\ 10^5$) was obtained osmometrically.

Measurement methods

Viscosity was measured with a capillary Ubbelohde viscometer adapted for gradual dilution at 25°C. Viscometric data were evaluated by Heller's extrapolation method. - Osmometric measurements were performed at 30°C using an automatic membrane Knauer osmometer. - Light scattering measurements were carried out with a Fica 40 000 photogoniodiffusometer in vertically polarized light with $\lambda = 546$ nm and in the angular range 30-150°. PVB solutions were left to dissolve at room temperature for c. 24 h and then purified either by pressure filtration through a glass filter Jena G5 or by centrifuging on a Beckmann L8-55 ultracentrifuge (rotor SW.1, 15000 r.p.m., 1 h). The scattering data were evaluated by the Zimm extrapolation method.- Refractometric measurements of the refractive index increments, dn/dc, were carried out using a differential refractometer Brice-Phoenix at 25°C and λ = 546 nm. Measurement of the $(dn/dc)_\mu$ values was preceded by an equilibrium dialysis. In dialyzers of a suitable design (9) the establishment of osmotic equilibrium between solution and solvent took at least 12 h.

Results and Discussion

PVB dissolves in a number of solvents which may be divided into two groups (cf.Fig.1), namely, "strongly H-bonded" and "moderately H-bonded" (10). A typical feature of dilute solutions of this copolymer ($c \leqq 0.5\%$ w/v) in all single solvents is a strong curvature of the scattering envelopes (Fig.2). In addition, the scattering data are greatly dependent on the history of the analyzed samples; they also are irreproducible, if dissolution takes place at elevated temperature. The molar mass determination by light scattering is extremely unreliable under these circumstances. The obvious cause is a certain, not too large fraction of copolymer aggregates. Unlike light scattering, these aggregates do not affect quantities ensuing from the

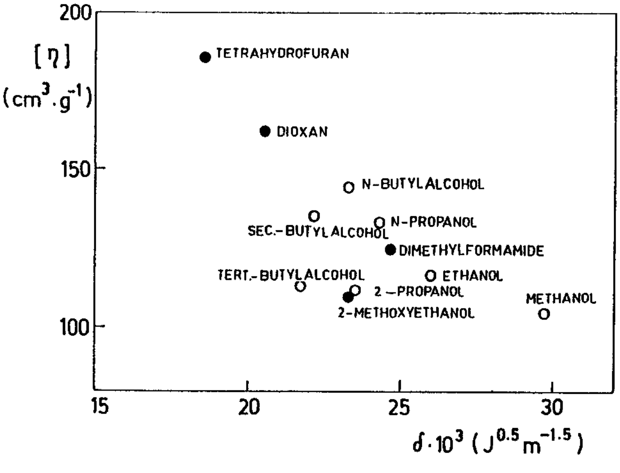

Fig. 1 Dependence of [η] on the dissolution parameter δ.
● moderately H-bonded, ○ strongly H-bonded solvent

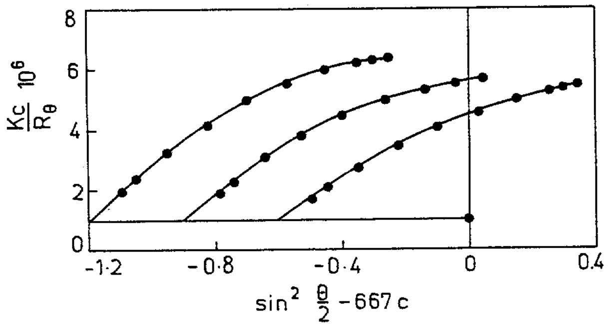

Fig. 2 The Zimm diagram of PVB in THF

measured concentration dependences of viscosity and osmotice pressure (Figs 1 and 3). Hence, in the case of PVB the intrinsic viscosity $[\eta]$ values along with those of the second virial coefficient obtained osmometrically may be used as a reliable criterion of the "solvent power" of the single solvent used.

We investigated the scattering behaviour of PVB in binary mixtures consisting of some solvents (subscript 1) given in Fig.1 and water (subscript 2) which selectively dissolves PVA. Since for the PVB under investigation water is rather a strong precipitant, the possible range of compositions of mixed solvents is comparatively narrow (volume fraction of the organic solvent ϕ_{10} varies in the range 0.7 - 1.0). We found that a decrease in the intensity of scattered light by ternary systems, particularly in the small-angle region, is brought about if PVB is dissolved direct in a mixture of higher alcohols (strongly H-bonded) with water (cf. Fig.4). This indicates the possible decrease in the weight of the dissolved particles. The presence of water in solvents from the "moderately H-bonded" group had an opposite effect on the scattering behaviour - the fraction of aggregates was increasing.

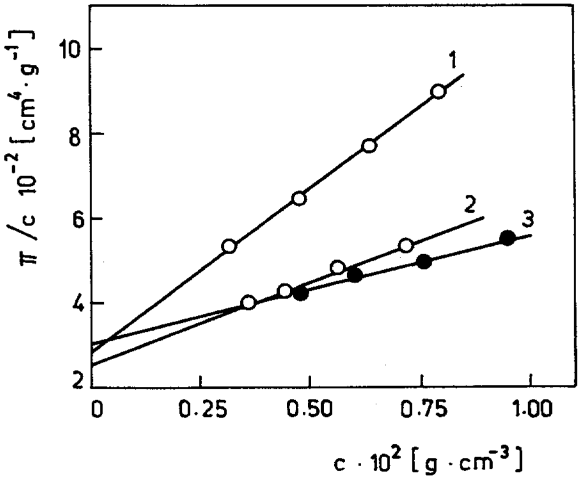

Fig. 3 Dependence of reduced osmotic pressure on concentration
1 THF, 2 2-ethoxyethanol, 3 methanol

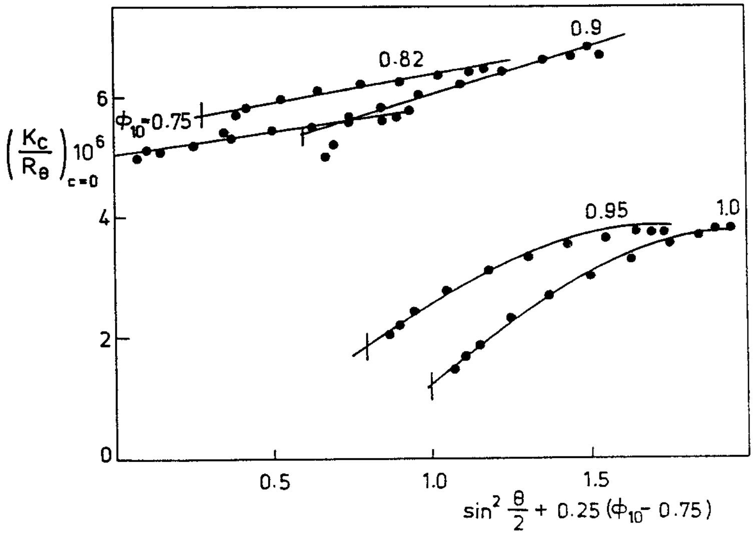

Fig. 4 Angular dependence of $(Kc/R_\theta)_{c=0}$ values depending on water content in 2-propanol

It may be assumed that each component of the mixed solvent solvates its own part of the copolymer macromolecule where it is preferentially sorbed. This gives rise to a difference in the composition of the mixed solvent inside ϕ_1 and outside the copolymer coil ϕ_{10}. Since the refractive indices of water and organic solvents differ from each other, the real refractive index increment does not correspond to the quantity determined in the traditional way, i.e. at a constant ratio between the individual solvent components, $(dn/dc)_k$. The correct molar mass is obtained from scattering data only by determining the refractive index increment measured at a constant chemical potential $(dn/dc)_\mu$, i.e. at the osmotic equilibrium between solution and solvent (11),

$$\frac{K'(dn/dc)_\mu^2 c}{R_0} = \frac{Kc}{R_0} = \frac{1}{M_w} + 2A_2c \quad , \qquad (1)$$

here, M_w is the mass average molar mass of the copolymer, c is its concentration, K and K' are optical constants, A_2 is the second virial coefficient, R_0 is the Rayleigh ratio extrapolated to zero angle. Hence, a quantitative investigation of desaggregation by light scattering was preceded by the determination of $(dn/dc)_\mu$ after an equilibrium dialysis of all ternary systems having the composition under investigation. The values of both refractive index increments are given in Fig.5. As follows from the dependence of M_w on ϕ_{10} (Fig.6), PVB can be molecularly dissolved in mixtures of tert.butyl alcohol (t-BuOH), 1-propanol (1-PrOH) and 2-propanol (2-PrOH) with water. The latest combination is optimal, as in the mixture of 2-PrOH with water PVB remains in the molecular form for ϕ_{20} in the range 0.1 - 0.25.

A quantitative measure of preferential sorption (difference between ϕ_{10} and ϕ_1) is the coefficient of preferential sorption (12), the value of which can be determined from the refractive index increments

$$\gamma = \{(dn/dc)_\mu - (dn/dc)_k\}/(dn_0/d\phi_{10}) \quad , \qquad (2)$$

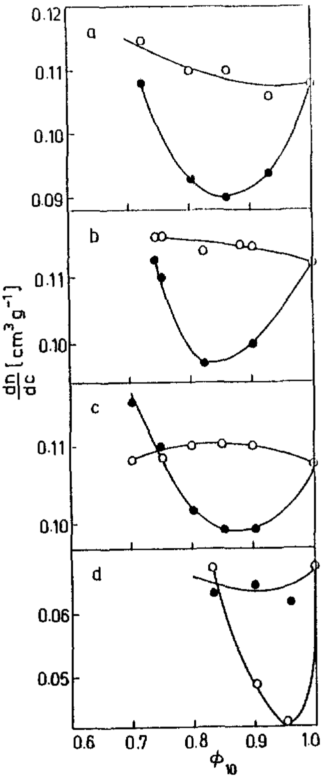

Fig. 5 Dependences of refractive index increment on composition of mixed solvent (volume fraction of organic component ϕ_{10}) : o $(dn/dc)_k$; ● $(dn/dc)_\mu$
a tert.butyl alcohol, b 2-propanol,
c 1-propanol, d dioxan

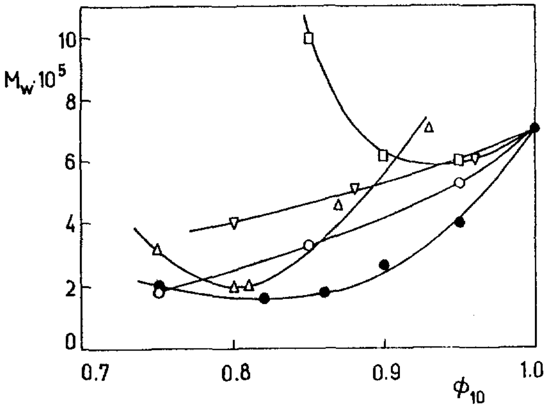

Fig. 6 Dependence of $\overline{M}_w$ values on composition of mixed solvent.
Δ t-BuOH, o 2-PrOH, o 1-PrOH, ∇ EtOH, □ dioxan

where $dn_o/d\phi_{10}$ is a change in the refractive index of the mixed solvent depending on its composition. The $\gamma = f(\phi_{10})$ dependences are given in Fig.7a. If solvents in the mixture with water are higher alcohols t-BuOH, 1-PrOH, 2-PrOH, water is preferentially sorbed on the PVB chain. As soon as the composition of the solvent $(\phi_{10})_i$ is in equilibrium with the sorption capacity of the chain, γ equals zero and the so-called inversion in sorption takes place - at $\phi_{10} < (\phi_{10})_i$ alcohol is preferentially sorbed. Also, $(\phi_{10})_i$ is the minimal volume fraction of alcohol in the mixture in which the PVB under investigation can still be visually dissolved. Inversion usually takes place immediately before PVB precipitates from solution. On the contrary, dioxan which represents the other group of the solvents is preferentially sorbed on the PVB chain from the mixture with water (Fig.7a). Its high affinity to vinylbutyral units obviously prevents water from access to the copolymer chain, thus impeding desaggregation. With increasing water content in dioxan, the fraction of aggregated PVB macromolecules also increases (Fig.6).

The degree of swelling of the copolymer coil which is a measure of the total sorption of the solvent can be seen from the dependence of intrinsic viscosity of the systems investigated in this study on ϕ_{10}. For the given

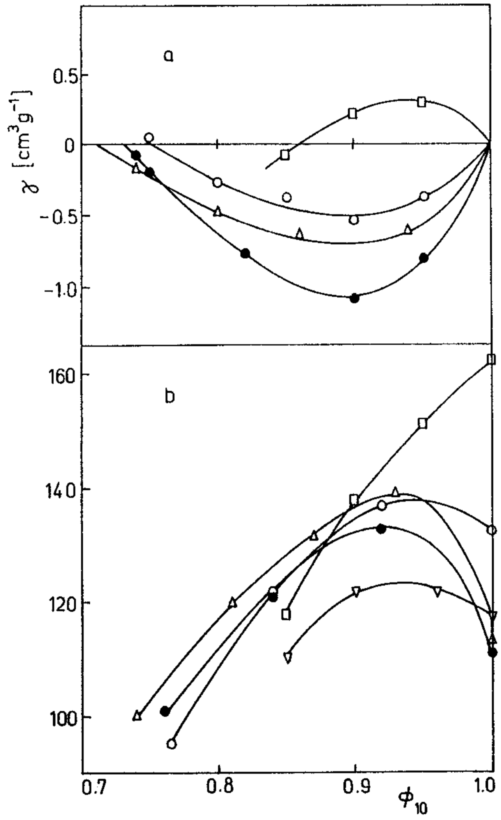

Fig. 7 Dependence of preferential sorption (a) and [η] (b) on composition of mixed solvent; meaning of symbols as in Fig. 6

combinations of alcohols with water, the function $[\eta] = f(\phi_{10})$ masses through a maximum; in the surroundings of the point of inversion $(\phi_{10})_i$ the degree of swelling of the coil is minimal, because $[\eta] \rightarrow [\eta]_\theta$ (8). In the case of dioxan the $[\eta]$ value decreases monotonically with increasing water content (Fig. 7b).

The results of experimental study allow us to infer that the suppression of formation of PVB and the decomposition of hydrogen bonds between macromolecules probably occur due to the simultaneous effect of several factors: 1) mechanism of dissolution which consists in the ability of both solvent components to create strong hydrogen bonds;

2) the resulting polarity of the dissolving mixture in which, together with water, the organic solvent having the dissolution parameter δ_S in the range $22 \div 26\ J^{0.5}m^{-1.5}$ also takes part;

3) the lowest possible solvation of the copolymer chain by the organic solvent $\chi_{1,cop} \rightarrow 0.5$, which makes possible an interaction between water and the vinyl alcohol component which in itself is very weak ($\chi_{2,PVA} \sim 0.494$; (13)).

This study may indicate a route for the characterization of a copolymer bearing groups which may prevent perfect solvation of the macromolecular chain without the necessity for a polymeranalogous transformation (7, 14).

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