Molecular Orientation and Young's Modulus of Plasticized and Nonplasticized Poly(vinyl Chloride)

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Synopsis

The Young's moduli of samples of poly(vinyl chloride) containing either no plasticizer or 5 pph of dioctyl sebacate were drawn uniaxially at 80°C to draw ratios, λ, in the range 1–3.3. The moduli, determined by a three-point bending method were found to increase monotonically with λ to a value of 6.3 GPa for the nonplasticized samples and to reach a maximum value of about 4.5 GPa for the plasticized samples above $\lambda = 2.3$, which showed voiding. The lower moduli of the plasticized samples for a given degree of orientation, as assessed from birefringence measurements, can be attributed to the diluent effect of the plasticizer on the load-bearing chains. The Raman measurements suggest that the crystallites probably orient rather like rigid rods in an affinely deforming matrix, with some relaxation.

INTRODUCTION

In previous studies[1,2] we have used Raman spectroscopy and measurements of birefringence to assess the degree of orientation in a variety of samples of plasticized and nonplasticized poly(vinyl chloride) (PVC) which were uniaxially oriented by drawing. In this paper we report similar studies on samples for which we have also measured the Young's modulus and we discuss the correlation between modulus and orientation.

THEORY OF THE RAMAN METHOD

The theory of the Raman spectroscopic method for studying orientation has been given in detail previously,[3] as has its application to PVC,[1,2] and it will be presented here only in outline. The results were expressed in the earlier work[1,2] in terms of average values of the Legendre polynomials $P_l(\cos \theta)$, where $P_0(\cos \theta) = 1$, $P_2(\cos \theta) = (3 \cos^2\theta - 1)/2$, $P_4(\cos \theta) = (3 - 30 \cos^2\theta + 35 \cos^4\theta)/8$, and θ is the angle between the draw direction and the chain axis. For complete orientation, all these averages are equal to 1.

The process of Raman scattering depends upon the change of polarizability of the chemical bond or group involved in a particular vibration with the movement of the atoms in question. Polarizability is a tensor quantity and the coefficients which relate the measured scattering intensities to the averages $\langle P_2(\cos \theta) \rangle$ and $\langle P_4(\cos \theta) \rangle$ involve the three principal components of the Raman tensor for the vibrational mode.[2] It is necessary to determine these
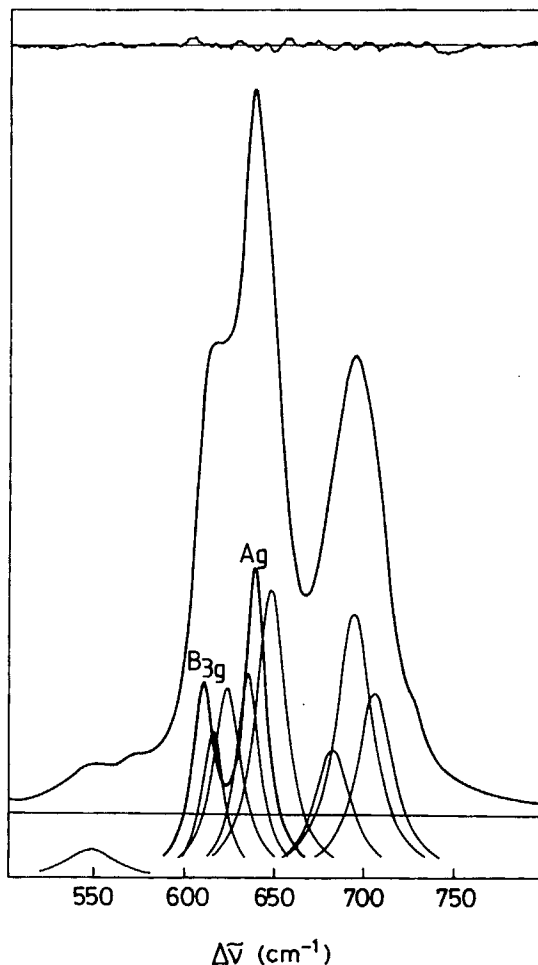
Fig. 1.   C—Cl stretching region of the Raman spectrum of PVC; fitted peaks, and background, their sum, and the difference between the sum and the original spectrum.

components or, more precisely, the ratios between them, in order to interpret the experimental data.

In the specific case of poly(vinyl chloride) it is reasonable to assume that the Raman tensors for the vibrational modes of chains in crystalline regions approximate to those deducible from symmetry considerations. The two obvious modes to study are those which give scattering at 608 and 638 cm^{-1}; they are the antisymmetric (B_{3g}) and symmetric (A_g) C—Cl stretching modes, respectively, of long syndiotactic sequences in crystalline regions.[4] Unfortunately, the peaks arising from these modes are overlapped in the Raman spectrum of commercial atactic PVC by those due to other configurational and conformational isomers and it is necessary to use curve fitting[4] in order to obtain quantitative intensity data (see Fig. 1).

In principal it is also possible to utilize scattering peaks, particularly those in the C—Cl stretching region, that are characteristic for chains in noncrystalline regions, and so obtain information about the orientation of these regions.

In practice, problems arise in determining the principal components of the appropriate tensors, but it is sometimes possible to proceed on the basis of reasonable assumptions. For example, the peak at 616 cm^{-1} is specific for short syndiotactic chains in the noncrystalline regions and it is possible to analyze the measured intensities on the assumption that the individual C—Cl bonds vibrate independently and that the Raman tensor for the vibration has cylindrical symmetry around the bond.[2]

In the present paper the results of Raman measurements on two series of drawn samples of PVC, plasticized and unplasticized, are presented and the values of $\langle P_2(\cos\theta)\rangle$ obtained are compared with the birefringences of the samples and the Young's moduli measured in the draw direction.

EXPERIMENTAL

Sample Preparation

The samples were made from a commercial PVC, M80/50, produced by BP Chemicals Ltd. Stabilizer (Mellite 381D) was added in the proportion of 4 parts to 100 by weight and for the plasticized samples 5 parts by weight of dioctyl sebacate were added. After mixing in a high speed mixer and milling between rollers the polymer was finally compression moulded to give a plaque approximately 2 mm thick. Further details of the preparation of similar plaques have been given previously.[1,4] Dumbbell-shaped specimens were milled from the plaques so that the central regions were 5 mm wide and these were drawn at 70°C in an Instron tensile tester at a draw speed of 1 cm/min. As soon as the required draw ratio was achieved the oven door was opened and the sample cooled to just above room temperature in about 40 s. The draw was homogeneous and, to a good approximation, uniaxial.

Refractive Index Measurements

The birefringences, Δn, of the samples were determined from retardations measured using a Zeiss-Jena microscope fitted with an Ehringhaus compensator and were subsequently corrected for the stabilizer and plasticizer content so as to reflect directly the orientation of the polymer chains. These values are called Δn_{corr}.

Modulus Measurements

The Young's moduli were measured using a three-point bending technique with a 10 s load, 110 s relaxation cycle. Sample lengths varying from 25 to 102 mm were used with loads varying from 25 to 100 g and the results were extrapolated to infinite length.

Raman Spectroscopy

The Raman spectra of a selection of the samples were obtained by scanning the region 520–776 cm^{-1} using a Coderg PHO Raman spectrometer with 90° scattering geometry. The exciting radiation was the 488 nm line from an argon ion laser. Eight spectra were obtained for each sample for different combinations of orientation of the sample and the polarization vectors of the incident

Sample	Draw ratio λ	Birefringence $\times 10^3$ Δn	Δn_{corr}	Young's Modulus E (GPA)	$\langle P_2(\cos\theta)\rangle_c$ Exact	Approximate
$U0$	1.00	—	—	3.56 ± 0.10		
$U1$	1.51	1.87	1.95	4.23 ± 0.15	0.18	0.19
$U2$	1.80	2.95	3.08	4.69 ± 0.15	0.22	0.25
$U3$	2.25	4.35	4.53	5.43 ± 0.18	0.35	0.34
$U4$	2.88	5.55	5.78	6.27 ± 0.20	0.22	0.24
$P0$	1.00	—	—	3.51 ± 0.18		
$P1$	1.20	0.51	0.57	3.45 ± 0.09		
$P2$	1.47	1.51	1.68	3.76 ± 0.07	0.11	0.11
$P3$	1.78	2.07	2.30	4.08 ± 0.07		
$P4$	1.96	2.55	2.83	4.27 ± 0.08	0.19	0.18
$P5$	2.28	3.18	3.53	4.60 ± 0.10	0.27	0.25
$P6$	2.57	3.72	4.13	4.57 ± 0.10	0.33	0.32
$P7$	2.62	3.91	4.35	4.51 ± 0.10		
$P8$	2.77	4.18	4.64	4.50 ± 0.10		
$P9$	2.93	4.52	5.03	4.58 ± 0.12		
$P10$	3.15	4.75	5.27	4.47 ± 0.10		
$P11$	3.29			4.58 ± 0.06		

and scattered radiation and these were combined to provide four independent spectra which were then fitted simultaneously to nine major peaks and four minor peaks by a least-squares fitting procedure to obtain the intensities of the 608 and 638 cm^{-1} peaks. These intensities were then used to calculate the values of $\langle P_2(\cos\theta)\rangle_c$ and $\langle P_4(\cos\theta)\rangle_c$ by the methods described previously,[1] where further details of the apparatus, the experimental procedure and the methods of analysis of the data may be found. The subscript c stands for crystalline material.

Unfortunately, it was not possible to obtain reliable measures of $P_4(\cos\theta)\rangle_c$ because of the lack of precise knowledge of the Raman tensors. The values of $\langle P_2(\cos\theta)\rangle_c$ are less sensitive and the most reliable values appeared to be those obtained from a simultaneous least-squares fit to the data for the A_g species peak for all samples, with the ratios of the Raman tensor components and the values of $\langle P_2(\cos\theta)\rangle_c$ and $\langle P_4(\cos\theta)\rangle_c$ for each sample as the unknowns. These are the values quoted in Table I under the heading "exact."

RESULTS AND DISCUSSION

Young's Modulus

Table I shows the draw ratios, birefringences, and Young's moduli of the samples; the U samples are unplasticized, the P samples plasticized. Figure 2 shows that the variation of modulus with draw ratio for both sets of samples is similar to that observed by other workers[5,6] for samples drawn at similar temperatures. The plasticized samples have a smaller modulus before drawing than the unplasticized samples and the difference increases monotonically with increasing draw ratio. The plasticized samples show an apparent satura-
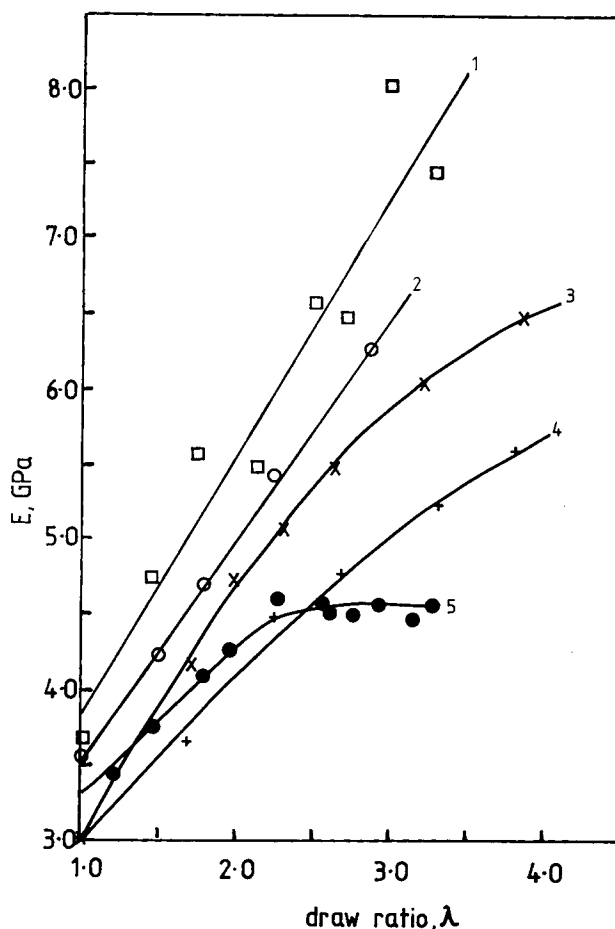
Fig. 2. Young's modulus, E, plotted against draw ratio, λ. (1) Ref. 5, samples drawn at 80°C; (2) Present work, unplasticized samples; (3) Ref. 6, samples drawn at 65°C; (4) Ref. 6, samples drawn at 110°C; (5) present work, plasticized samples.

tion of modulus at a draw ratio of about 2.25, which is associated with the onset of a milky appearance due to voiding.

Figure 3 shows that the birefringence of a drawn plasticized sample is also lower than that of an unplasticized sample drawn to the same draw ratio, but the onset of voiding for the plasticized samples is not reflected in the birefringence data as it is in the modulus data. Since the birefringence is a measure of the overall chain orientation, this suggests that the true modulus of the polymer, after correction for voiding, would continue to rise beyond the draw ratio 2.25.

Fig. 4 shows that the plasticized samples have a lower modulus than the unplasticized samples for the same overall molecular orientation, as indicated by the birefringence, and that until the voiding region is approached the difference is about 5%. This further supports the idea the true modulus of the plasticized samples probably continues to increase within the voiding region and also suggests that the main effect of the plasticizer on the modulus is via its dilution of the polymer chains, which alone can sustain tensile forces.
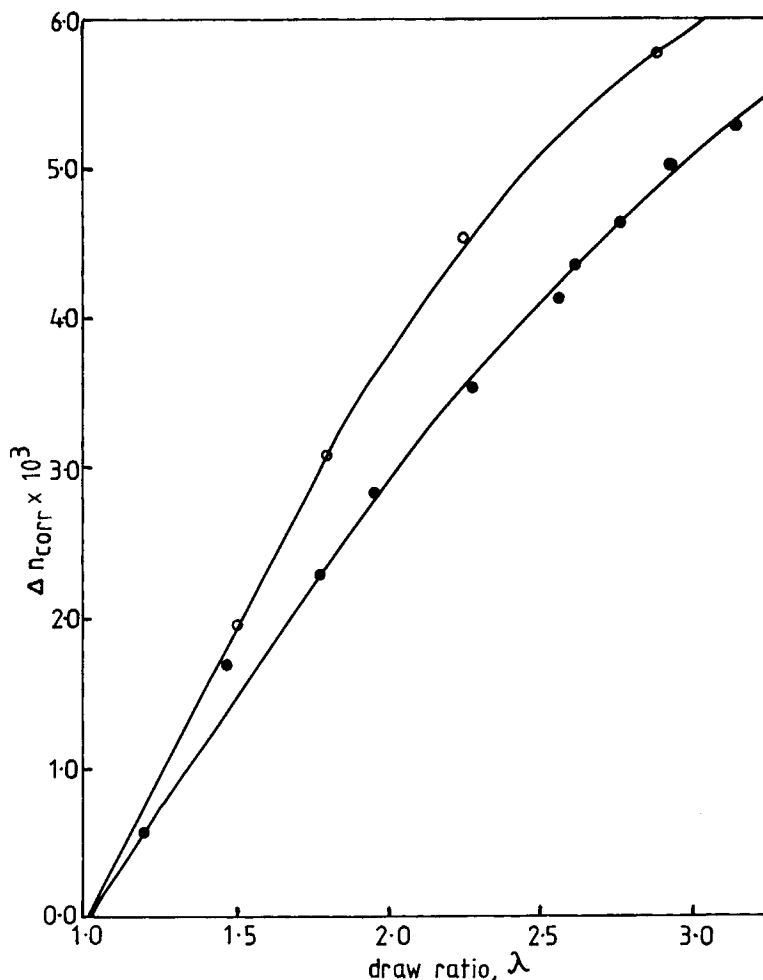
Fig. 3. Corrected birefringence, Δn_{corr}, plotted against draw ratio, λ. ($\circ$) Unplasticized; ($\bullet$) plasticized.

To test the latter idea, the volume fraction of plasticizer in the plasticized samples was estimated from the measured densities of the plasticized and unplasticized samples. The moduli of the plasticized samples were then "corrected" by dividing them by the volume fraction of PVC plus stabilizer. The results, which are shown in Figure 4 for those samples that did not show voiding, support the idea that the plasticizer acts simply as a diluent to the polymer in determining modulus for a given degree of orientation. A similar correction for voiding could not be made because of the difficulty of determining the densities of voided samples.

Orientation Distribution

The birefringence is proportional to $\langle P_2(\cos\theta)\rangle_a$, where the subscript a denotes the average over all chains, whereas the values of $\langle P_2(\cos\theta)\rangle_c$ are averages only over the crystalline chains. Figure 5 shows that there appears to
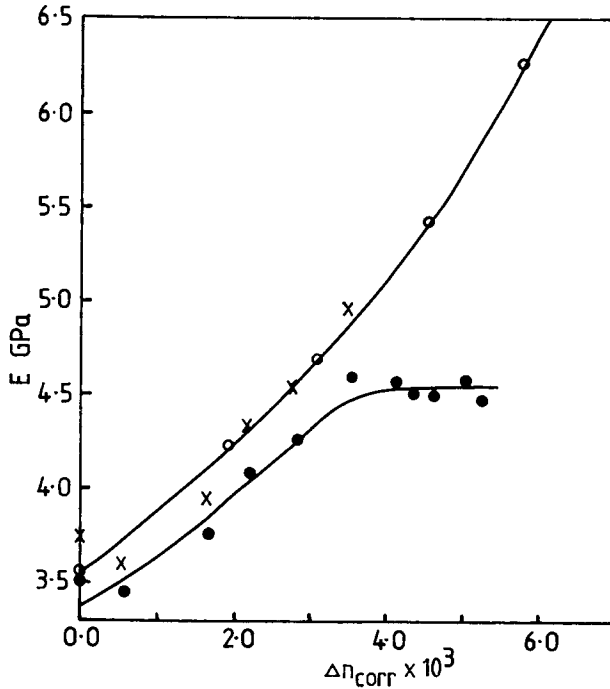
Fig. 4. Young's modulus, E, in draw direction plotted against corrected birefringence, Δn_{corr}. (○) Unplasticized; (●) plasticized: (x) plasticized but "corrected."

be a unique relationship between $\langle P_2(\cos\theta)\rangle_c$ and Δn_{corr}. If this relationship is the straight line shown, it follows that the chains in the crystallites have the same degree of molecular orientation as the chains in the noncrystalline regions and that the birefringence for full orientation is 13.3×10^{-3}. This is in good agreement with the value 13.0×10^{-3} deduced earlier[1] using a similar linear extrapolation on data for a series of samples drawn at 22°C, for which arguments were given suggesting that the crystalline and amorphous chains orient together at this temperature.

If, however, the relationship between $\langle P_2(\cos\theta)\rangle_c$ and Δn_{corr} is given by the curve shown in Figure 5 it follows either that Δn for full orientation is appreciably less than 13.3×10^{-3} and that the chains in the crystallites are somewhat less oriented than average at all orientations, or that the value of Δn for full orientation is close to 13.3×10^{-3} and the chains in the crystallites are somewhat less oriented than average at low orientations and more highly oriented than average at high orientations. This may be consistent with the suggestion that at low degrees of orientation in PVC the a axes of the crystallites are preferentially oriented toward the draw direction and that c-axis orientation only takes over at higher draw ratios.[7] This might also explain the shape of the modulus versus Δn_{corr} curve, since a more rapidly increasing crystallite c-axis orientation with increasing overall orientation would be expected to lead to a more rapidly increasing modulus, as observed. If reliable values of $\langle P_4(\cos\theta)\rangle_c$ could be obtained it is possible that they would throw some light on this question by giving a more precise indication of the form of the distribution of orientations.
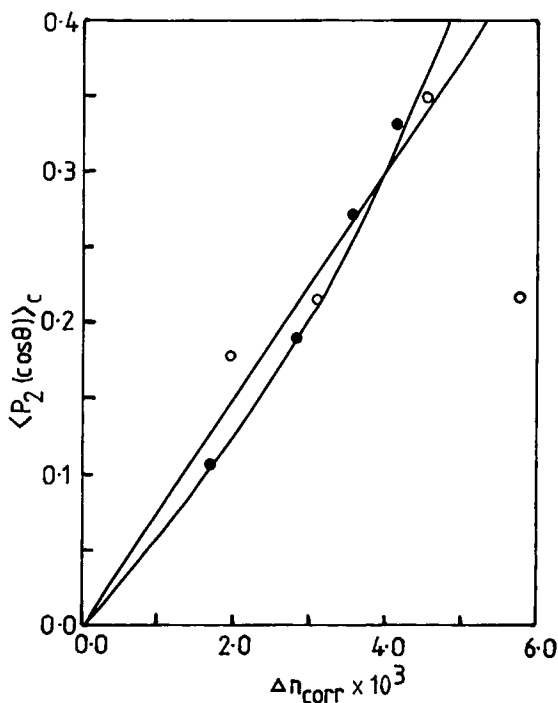
Fig. 5. $\langle P_2(\cos\theta)\rangle_c$ plotted against corrected birefringence, Δn_{corr}. (○), unplasticized; (●) plasticized.

As found previously,[2] values of $\langle P_2(\cos\theta)\rangle$ determined from the intensities of the 616 cm^{-1} peak were somewhat higher than the corresponding values of $\langle P_2(\cos\theta)\rangle_c$, again suggesting that short syndiotactic segments are more highly oriented than the crystalline chains.

Comparison with Models for Orientation

It is instructive to compare the values of $\langle P_2(\cos\theta)\rangle_c$ with those predicted by the pseudoaffine rigid-rod rotation model.[8] Figure 6 shows this comparison. Curve a is the direct prediction of the model and curves b and c are obtained from curve a by replacing the draw ratio, λ, by an effective value equal to $1 + (\lambda - 1)/\alpha$, where $\alpha = 1.64$ or 2.29 for curves b and c, respectively. Although the data are rather limited, it is tempting to conclude that the parameter α measures the degree of relaxation during drawing and that the pseudoaffine mechanism applies to the orientation of the crystallites embedded in the continuous medium of the noncrystalline chains.

A Simpler Calculation of $\langle P_2(\cos\theta)\rangle_c$

The method of calculating $\langle P_2(\cos\theta)\rangle_c$ from the Raman data as described above is quite time consuming because of the curve fitting of the spectra. We find, however, that the following simplified method gives results which may be acceptable, at least up to the degree of orientation found here.
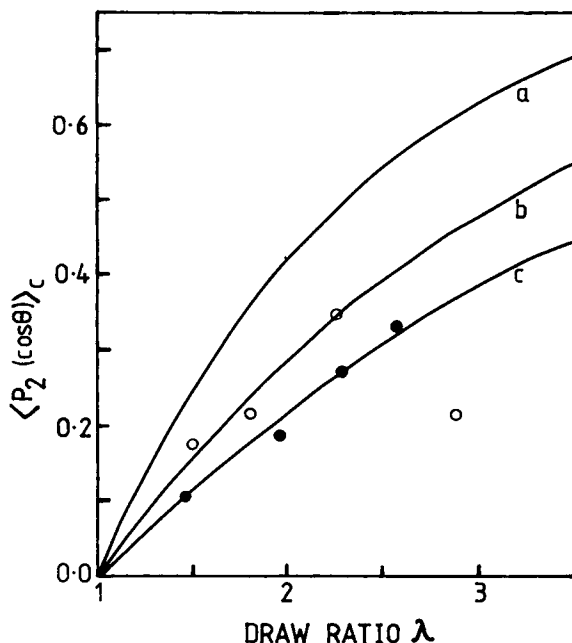
Fig. 6. $\langle P_2(\cos\theta)\rangle_c$ plotted against draw ratio, λ. See text for explanation of curves.

The intensity at 640 cm^{-1}, close to the position of the A_g peak, is determined from each observed spectrum after subtraction of a linear background but without curve fitting. The four independent intensities so obtained are used, together with the values of the ratios of the Raman tensor components found in the fits referred to earlier, viz. 1 : 0.368 : 0.185, in Eq. (4) of Ref. 1 to find values of $\langle P_2(\cos\theta)\rangle_c$ as described there. These values are multiplied by the empirical factor 1.27. Values obtained in this way are shown in the last column of Table I.

CONCLUSIONS

It is not easy to apply the Raman technique to the study of orientation in PVC because of the difficulty of extracting the intensities of the individual Raman peaks and because the forms of the Raman tensors are not precisely known. Nevertheless, if it is used in combination with other measurements useful information may be obtained about the distribution of orientations.

It is clear from the results that the overall molecular orientation attained in the present work is not very high and it seems likely that if higher orientation were to be attained the value of the modulus might be quadrupled over its value for the unoriented samples. The use of a greater concentration of plasticizer might enable greater draw ratios to be achieved, but it is not clear that this would lead to a greater modulus, even if voiding did not occur, unless the plasticizer were subsequently removed. The drawing of PVC gels and the subsequent removal of the solvent should prove an interesting study in this context.

References

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