Gelation/crystallization of poly(vinyl chloride)

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Introduction

The existence and origin of crystallinity in PVC is still a matter of debate, despite the fact that this particular polymer has a long manufacturing history, being one of the major bulk polymers produced today. Certainly, the presence of crystallinity cannot be denied for those PVC samples which have been prepared by special techniques, like polymerization in the presence of aldehydes\(^1,\!^2\) or urea\(^3,\!^4\) and low temperature polymerization\(^5\), where crystallinity is related to the presence of relatively long syndiotactic sequences in the polymer chains.

The question remains however, whether these observations can be extrapolated to PVC types produced on a commercial scale by, for instance, an emulsion or suspension polymerization process. From \(^{13}\text{C}\) n.m.r. results, it was concluded that these commercially produced PVC's are mainly atactic. The isotactic (mm), heterotactic (mr) and syndiotactic (rr) triads are found to be of the order of 0.2, 0.5 and 0.3 respectively\(^6,\!^8\). Taking these data into account one would not expect a measurable amount of crystallinity to be present in bulk PVC. However, the values for crystallinity of standard PVC types which are reported in the literature vary between 0 and 20\%, based on various experimental data and interpretations\(^7\).

The large spread in values for the degree of crystallinity is related to the difficulties encountered in quantitative interpretation of the X-ray, i.r. and d.s.c. data obtained from solid PVC samples.

Crystallization from solution usually enhances crystallinity, and it has been reported in the literature that upon cooling of moderately concentrated PVC solutions, thermoreversible gelation occurs. This gelation phenomenon was interpreted in terms of a crystallization process, probably of the fringed micellar mode\(^8,\!^9\). Upon stretching these PVC gels, rather well-pronounced X-ray diffraction patterns were obtained\(^8\).

This finding demonstrates that PVC, despite its nearly atactic character, is capable of forming a certain amount of crystallinity, but this does not imply that the initial step of the gelation process is a crystallization phenomenon. To investigate the role of crystallization in this gelation process we chemically modified PVC by post-chlorination. The kinetics of gel formation was studied as a function of chlorine content by measuring the increase of the storage modulus as a function of time in a similar way as described in ref. 9.

Experimental

Materials. Varlan S7120, a suspension-polymerized PVC from DSM, having a \(M_w\) of 105 000 g/mole and a \(M_w\) of 55 000 g/mole, was used as the reference material. This particular PVC sample was chlorinated, in solution and directly as a powder.

Solution-chlorination: The polymer powder was dispersed in tetrachloroethane (TCE) at room temperature, concentration 5 g/100 ml. The suspension was flushed with \(\text{N}_2\) and heated in an oil bath, with stirring. After complete dissolution of the PVC polymer, chlorine gas was passed through the solution at 125°C.

No initiator nor u.v. radiation was used to initiate the chlorination reaction.

At regular intervals, aliquots of the (C)PVC/TCE solutions were transferred to a separate vessel. After chlorine gas removal by \(\text{N}_2\) flushing, the different solutions were precipitated in methanol.

The (C)PVC samples precipitated quantitatively as a gelly mass. After filtering and preliminary drying, the precipitated mass was redissolved in tetrahydrofuran (THF), after which diethyl ether was added to the (C)PVC/THF solution until the mixture became hazy. These mixtures were added dropwise to vigorously stirred cold (about 0°C) methanol.

Using these procedures, a finely divided powder was obtained.

After filtering and vacuum drying, the chlorine content was measured, using the standard Schöniger method.

Power-chlorination: In a rotating glass cylinder equipped with a thermostated i.r. heating system, PVC powder was tumbled for at least half an hour at room temperature. After that period the system was heated to about 125°C and chlorine gas was passed through the system at a constant flow rate.
At time intervals ranging from 10 to 60 min, the chlorine was removed by flushing the system with \( \text{N}_2 \) and samples were isolated. Their chlorine content was determined from the weight increase and by the Schöniger method.

Table 1 summarizes the samples obtained by the solution and powder chlorination procedures, respectively.

Techniques. Gelation kinetics: The PVC and CPVC samples were dissolved in di-(2-ethylhexyl)phthalate (DOP) at 160°C. Stabilizers were added and \( \text{N}_2 \) flushing was used during the dissolution procedure. The solutions were poured directly into the measuring cell of a viscometer (Rheometrics RMS-7200).

The storage modulus \( G' \) and the loss angle delta were measured as a function of the oscillation frequency and time at 23°C. The molar concentration of the CPVC and PVC/DOP solution was kept constant at 1.6 mol l\(^{-1}\).

\(^{13}\text{C} \) n.m.r.: The \(^{13}\text{C} \) n.m.r. spectra of the CPVC and PVC samples were obtained at 25.2 MHz using a Varian XL-100/15 spectrometer.

The sample concentration was about 10% w/v in a solvent mixture of 1,2,4-trichlorobenzene and perdeuterated benzene (internal lock). Using 12 mm tubes the spectra were recorded in the mixed solvents at 85°C using pulse widths of 35 s (pulse angle 77°) and pulse delays of 2 s. Spectra were generally obtained after the accumulation of 25000 scans (corresponding to a spectral width of 3000 Hz/digital resolution 0.667 Hz/pt). Peak areas were determined using a planimeter and assuming no differential NOE's and \( T_1 \)'s to occur; see also refs. 10 and 11.

Results and Discussion

Figures 1, 2 and 3 show the frequency dependence of the storage modulus \( G' \) and the loss angle (delta) as a function of oscillation frequency and time for different samples.

Table 1 PVC and CPVC samples

<table>
<thead>
<tr>
<th>Type/code</th>
<th>Chlorine content % w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>Reference PVC S-7120 56.8 (theoretical)</td>
</tr>
<tr>
<td>(B)</td>
<td>Powder-chlorination 62</td>
</tr>
<tr>
<td>(C)</td>
<td>Powder-chlorination 65</td>
</tr>
<tr>
<td>(D)</td>
<td>Solution-chlorinated 57.5</td>
</tr>
<tr>
<td>(E)</td>
<td>Solution-chlorinated 58</td>
</tr>
<tr>
<td>(F)</td>
<td>Solution-chlorinated 59.5</td>
</tr>
<tr>
<td>(G)</td>
<td>Solution-chlorinated 60.6</td>
</tr>
</tbody>
</table>

Figure 1 Storage modulus \( G' \) and loss angle \( \delta \) vs. frequency for sample A as a function of time, a=3; b=6; c=10; d=21; e=42 min and f =16 h

Figure 2 Storage modulus \( G' \) and loss angle \( \delta \) vs. frequency for sample B as a function of time, a=3; b=5; c=10; d=21 and e=42 min
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Figure 3 Storage modulus $G'$ and loss angle $\delta$ vs. frequency for sample G as a function of time, $a=3$; $b=5$; $c=8$; $d=21$ and $e=53$ min of time for three selected samples A, B and G. It can be concluded from Figures 1 and 2 that the PVC reference sample A and sample B build up an elastic network in DOP as shown by the appearance of a plateau region in the $G'$ vs. frequency plots and the values for the loss angle delta extrapolated to low frequencies.

In contrast, the solution-chlorinated sample G in DOP remains a fluid and no sign of any network formation is present.

Some semi-quantitative information regarding the kinetics of gel formation can be obtained by plotting the value for $G'$ at log $\omega=0$, vs. log time (Figure 4). Once more a striking difference is seen between the solution-chlorinated vs. the powder chlorinated PVC samples. This difference is well illustrated by plotting the value for the pseudo-equilibrium modulus $G_e$ at $t=60$ min as a function of the chlorine content. In Figure 5 a gradual decrease in the value for $G_e$ is observed for the powder-chlorinated samples in contrast to a rapid fall in the $G_e$ moduli for the solution-chlorinated samples. At about 60% w/w chlorine, the solution-chlorinated samples completely lose their gel formation ability. This chlorine content corresponds to a conversion of about 13 mole % monomer units containing one additional chlorine atom each (see Appendix).

It is well known that chlorination of PVC and PE in solution results, at least in the early stages of the process, in an approximately random introduction of chlorine in the polymer chain and no significant amount of $-\text{Cl}-\text{Cl}$ formation. On the contrary, chlorination of PVC powder is a non-random process. It was reported recently on the basis of $^{13}$C measurements, that during chlorination of PVC powder the amount of syndiotactic sequences remains practically unchanged. If it is assumed that the crystallization of PVC results from the presence of a small amount of syndiotactic sequences of sufficient length to form microcrystallites, then the differences in gelability of the solution and gas phase chlorinated samples respectively, could be easily explained as follows. During the chlorination of PVC powder the chlorine molecules are excluded from the microcrystalline domains already formed during the polymerization process, which, as stated above, are supposed to consist mainly of syndiotactic sequences. On the contrary, solution-chlorination randomly attacks the whole polymer chain.

Figure 4 Storage modulus $G'$ at 1 Hz vs. gelation time at 23°C for various samples, for explanation see Table 1.
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Figure 5 Dependence of storage modulus $G'_s$ (at $t=60$ min) on chlorine content for various samples

and a minor amount of additional chlorine in the macromolecule is sufficient to decrease the average syndiotactic sequence length below a minimum value necessary for crystallization.

This explanation, although being very attractive, lacks firm experimental evidence. The existence of relatively long syndiotactic sequences in commercially produced PVC/s is rather unlikely. Secondly, the interpretation of the $^{13}$C n.m.r. spectra of chlorinated samples cannot be performed in a quantitative way. Figure 6 shows spectra of powder-chlorinated PVC’s as a function of % w/w chlorine. At first glance the $rr$ triad resonance peak increases relatively at the expense of the isotactic (mm) and heterotactic absorptions (mr). However, recently Komorowski et al.11 showed the presence of severe overlap between the various peaks in the $^{13}$C n.m.r. spectra of CPVC samples as shown clearly for instance in Figure 6C.

Consequently it is impossible to deduce quantitative information from the spectra with respect to the preservation of certain tactic sequences. The results of tests on the samples obtained by chlorinating PVC powder with respect to the gel formation kinetics and the gradual decrease in the value for $G'_s$ with increasing chlorine content could equally well be explained in terms of a heterogeneous chlorination process with excess surface chlorination of primary PVC particles at the expense of relatively unaltered inner parts of PVC.

Summarizing, the concept of chlorination of PVC aids in understanding the mechanism of gel formation and reaffirms the relation between gel formation and crystallizability, but no firm conclusion can be drawn with respect to the origin of crystallinity in commercial PVC samples. Further investigations, including fractionation experiments, are needed to answer the question whether crystallization is mainly due to specific tactic sequences or a co-crystallization process, an issue raised some time ago13 and reconsidered recently by Guerrero and Keller14.

Figure 6 $^{13}$C n.m.r. spectra of PVC (sample A) and chlorinated PVC powder (B and C corresponding to Table 1)

Appendix

Assuming no $-CCl_3-$ formation the relation between the fractional conversion $x$ vs. the % Cl (w/w) $X$ is given by:

$$x = \frac{(62.5X - 3350)}{(35.5 - 0.345X)}$$

In equation (1) $x$ is the percentage of (base) molar units containing one additional chlorine atom.

Acknowledgement

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We are indebted to Professor A. Keller (Bristol University) for stimulating discussions.

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A new look at the enhanced low-angle scattering in moderately concentrated polymer solutions

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In the light of the recent discovery by Tan et al. of the gelation ability of some atactic polystyrene solutions at low temperature above the UCST, we reexamine the enhanced scattering observed at small angles in moderately concentrated solutions. In this communication we present some results gained from light scattering experiments showing that there seems to be a correlation between these two phenomena: i.e. no abnormal scattering effect when dealing with a solvent preventing gelation whereas abnormal scattering when using a solvent promoting the gelation. The results are discussed and a tentative explanation is given.

Keywords Light scattering; physical gelation; atactic polystyrene; concentrated solutions; decalin; toluene; chloroform; methyl-ethyl ketone; 1,2-dichloroethane

Introduction

Some years ago, the scattering of light by moderately concentrated solutions of polymers was intensively investigated mainly in order to evaluate the concentration effect on the chain dimension. Unexpectedly, instead of obtaining a linear variation from a Zimm representation as in dilute solutions, two types of behaviour were observed. While at larger angles the slope of the straight curve remains constant, at smaller angles a downturn appears, the average slope of which becomes steeper and steeper with increasing concentration. This abnormal and unpredicted effect was first imputed to either ill-removed dust or insoluble material. However, it was demonstrated that this phenomenon is genuine and characteristic of particular mixtures of polymer–solvent. Paradoxically, the phenomenon arises for good solvents and tends to vanish for θ-solvents at the θ temperature.

Recently, Tan et al. have succeeded in preparing true thermoreversible gels from atactic polystyrene (APS) solutions without quenching under the spinodal curve. Basically, the gels are obtained from moderately concentrated solutions cooled down to low temperature (typically 0°C to ~ -100°C). From d.s.c. experiments, it is obvious that the gelation does not necessarily occur whatever the solvent. Some solvents, in spite of their ability to remain liquids down to very low temperatures, do not allow the polymer solution to gel.

In the light of the Tan et al.’s findings, we shall try to discover whether there is a correlation between the abnormal scattering effect and the gelation ability of uncryscalizable polymers. As a matter of fact, some solvents producing the gelation are known to give rise to abnormal scattering at small angles. This communication is intended to report preliminary investigations performed through the use of a light scattering technique on moderately concentrated polymer solutions using some of the solvents featuring in the study of Tan et al.

We have especially aimed at discovering whether the solvents, wherein any physical gelation is absent, exhibit the scattering effect at small angles.

Experimental

Solvents. For this study, five different solvents have been employed. Concerning those wherein gelation can occur, we chose methyl-ethyl ketone (MEK) and toluene. Both these solvents are known to give rise to the scattering effect. Thus, they have provided a way of comparing experimental data obtained from them with those obtained from the solvents in which gelation of APS is not observed. In this latter case, three solvents have been used, characterized by a very low freezing point (see Table 1) namely; decalin, 1,2-dichloroethane and chloroform. As no hint is available in Tan’s paper as to the composition of trans and cis isomers of the decalin, we took a mixture 55% cis and 45% trans.

The low freezing point is an important parameter, as the gel may form at very low temperature. As an example, benzene which gives rise to the scattering effect is said to be a non-gelation solvent. This does not seem surprising since the freezing point of this solvent is near 5°C. Had it had a lower freezing temperature, then gelation might have been possible.

All the solvents are characterized by a high purity grade. Special care was taken with chloroform which was of i.r.-spectroscopy grade. It contained 2% alcohol as stabilizer that had been washed with distilled water, which was then removed by decantation and finally distilled so as to give chloroform that was free of impurities.

It is worth mentioning that in all these solvents the atactic polystyrene exhibits a high contrast factor (dn/dc)