

An n.m.r. and d.s.c. investigation of the solubility conditions of didecylphenylphosphite in rigid poly(vinyl chloride)

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It is shown from n.m.r. measurements that didecylphenylphosphite used as a thermal co-stabilizer is not completely dissolved in rigid poly(vinyl chloride) (PVC). D.s.c. measurements however, show a marked effect on the glass transition temperature of PVC, which implies that the co-stabilizer is dissolved to some degree in the PVC phase. Although this effect on the glass transition temperature proceeds continuously with the added amount of the co-stabilizer, d.s.c. measurements alone cannot give a full description of the solubility conditions. Nor can the effects observed by d.s.c. be used to give criteria for a complete solubility.

(Keywords: rigid PVC; impact-modified PVC; didecylphenylphosphite; solubility conditions; wide-line nuclear magnetic resonance spectroscopy; differential scanning calorimetric spectroscopy)

INTRODUCTION

It has been observed in earlier investigations that didecylphenylphosphite (CH 300, Ciba-Geigy), when investigated in a compound polymer matrix of PVC and impact modifier, does not dissolve completely but is distributed between an impact modifier phase and a rigid PVC phase. This observation has aroused suspicion regarding the completeness of the solubility of CH 300 in samples where PVC constitutes the only polymer component. The main effort has therefore now been devoted to such systems where no other pure component than CH 300 gives rise to a narrow line at temperatures up to room temperature. It has been our intention to study the distribution of the costabilizer between the rigid PVC phase and the liquid costabilizer phase as a function of the amount of added CH 300. For stabilization of the PVC polymer a 'base' stabilizer of barium-cadmium laurate with synergistic addition of pentaerythritol has been used and in earlier studies such stabilizers have been shown to give rise to only broad n.m.r. lines at room temperature.

The aim of the work has also been to investigate how additions of CH 300 can also influence the transition temperature of PVC. As discussed in earlier studies, wide-line n.m.r. is not very suitable for such measurements since it is slow and since measurements have to be made somewhat above the glass transition temperature of PVC. The phase relations for this type of systems are appreciably changed by such heat treatment. We have therefore made use of wide-line n.m.r. for the investigation of soft components of systems where measurements have been made at room temperature and lower temperatures. D.s.c. has been used for the investigation of the rigid PVC phase where measurements have been made with comparatively rapid sweeps of the temperature from 250 K up to 380 K.

EXPERIMENTAL

The measurements were performed using a PVC-polymer (S 658, Kema Nord AB, Stenungsund, Sweden) with $M_w = 84\,000$. The pure PVC-polymer was mixed with 0, 1, 2, 4, 6 and 10 parts per hundred didecylphenylphosphite (CH 300, Ciba-Geigy) and 2 pph barium-cadmium laurate with the synergistic addition of pentaerythritol (BC 26, Ciba-Geigy). Samples in the powdered and the rolled form were investigated. Before the rolling procedure the polymer component in the powdered form and the stabilizers were mixed at 110°C for 20 min using a rotation stirrer run at constant speed.

All the rolled samples were prepared at the laboratory of Kema Nord AB, Stenungsund, Sweden. The rolling temperature was $170^\circ \pm 1^\circ\text{C}$ and the friction ratio between the rolls was chosen at 1:1. Sample thickness was approximately 1 mm, and the samples were cooled between two metal plates directly after the rolling.

Calorimetric measurements were performed with a Perkin Elmer differential scanning calorimeter, DSC-2. The thermograms were obtained using $20^\circ\text{C min}^{-1}$ heating rate from 250 K–380 K and $320^\circ\text{C min}^{-1}$ cooling rate directly after the upper temperature limit was reached. The sensitivity was 1 mcal s^{-1} . Sample weights were $10.0 \pm 0.2\text{ mg}$ and aluminium was used as reference.

The thermograms were recorded in such a way that a nearly horizontal base-line was obtained between 290 and 310 K. The glass transition temperature (T_g) was taken at a mid-point in the thermogram as measured from the extension of the pre- and post-transition base-lines. We assume here that the heat capacity change is half the value of this change upon going through the transition (see *Figure 1*). This technique in measuring T_g has been reported to be the most reliable and reproducible¹. The apparatus was calibrated with Indium.

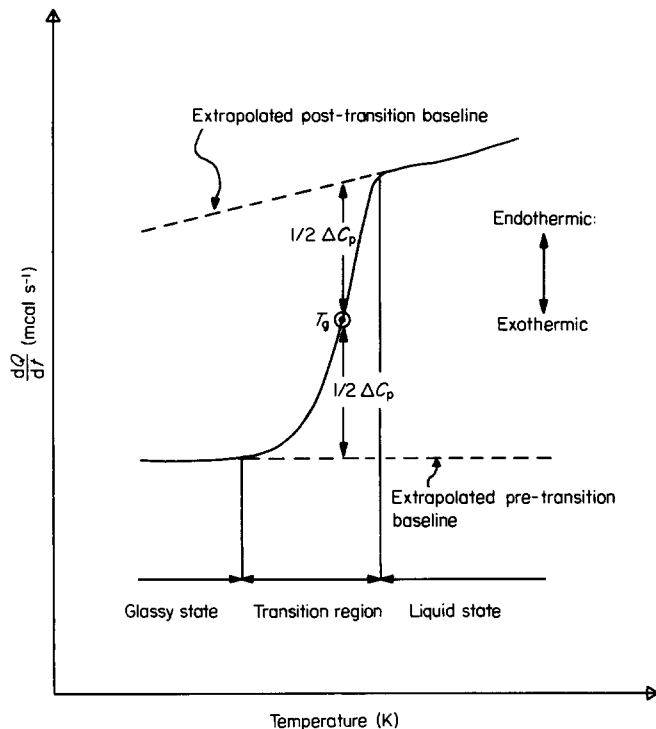


Figure 1 Measurement of the glass transition temperature (T_g). A schematic representation of the d.s.c. curve for PVC. (○ indicates the estimated glass transition temperature)

The broad line n.m.r. measurements were performed in a similar fashion to those of earlier studies²⁻⁴. A reduced quotient k/k_s was used, where k stands for the quotient between the narrow and the broad line peak-to-peak amplitude of the sample corresponding to the soft CH 300 phase and the rigid PVC phase respectively. k_s represents the corresponding quantity for a standard sample of a pure graft polymerized powder blend containing 8 wt% EVA (Ethylene-vinyl acetate copolymer with 45 wt% vinyl acetate, Levapren 450 P, Bayer AG, West Germany), where vinyl chloride is suspension polymerized with lauryl peroxide as initiator at 60°C. The spectrum from this standard sample was recorded each day when measurements were performed. Effects of long time variations due to instabilities of the instrument are thus reduced.

X-ray measurements on the phosphorus content in the samples showed an accuracy within 2.65% regarding the amount of added didecylphenylphosphite, and that the phosphorus content did not depend on the rolling time.

RESULTS AND DISCUSSION

For all samples containing CH 300 a narrow line component was observed at room temperature together with the broad line originating from the PVC-phase and the other additives. As CH 300 is in liquid form at room temperature (where the wide-line n.m.r. measurements were performed) it is obvious that the narrow line originates from CH 300 in its liquid state. Since the narrow line component was observed well resolved from the broad line for samples with a content of CH 300 down to 1.0% it must be concluded that, even at this low concentration, only a part of the CH 300 is dissolved in the rigid PVC phase.

The results of the n.m.r. measurements are shown in

Figure 2, where a quotient of the line amplitudes of the recorded narrow and the broad line components are presented as a function of the amount of CH 300. The largest quotients were observed for the powdered samples, which were all prepared by mixing for 20 min at 110°C. This implies that for this type of samples the largest contribution is from the CH 300 phase. The quotients are appreciably reduced upon rolling of the samples for 5 and 15 min. We conclude that a measurable amount of CH 300 is dissolved in the PVC-matrix by this treatment. The effect seems to be somewhat larger in the case of the prolonged rolling for 15 min compared with rolling for 5 min.

Results of the calorimetric measurements are shown in Figure 3 and typical examples of thermograms are presented in Figure 4 where the measured T_g for each curve is shown. It is seen from these Figures that the T_g of PVC is decreased continuously with increased addition of CH 300. As a consequence of this phenomenon we must conclude that the amount of dissolved co-stabilizer increases with the amount of co-stabilizer added. N.m.r. data, however, show also that the CH 300 phase intensity increases, which implies that the co-stabilizer is distributed between the phases. The shape of the uniform and sharp PVC-transition does not seem to be affected by the additive, and we have not been able to observe any broadening or any shifting in separate regions. It is seen from Figure 3 that T_g is somewhat lower for the powdered samples so we would like to assume that the degree of entanglement is lower in such samples due to their porous structure.

This fact has at a first glance appeared surprising to us since the n.m.r. results indicate that CH 300 is dissolved in the PVC-matrix to a lower degree in the powdered samples. These effects could, however, be explained by assuming that the porous structure of the powdered samples implies that a certain amount of dissolved CH 300 increases the segmental mobility of the polymer chains to a higher degree compared with the rolled

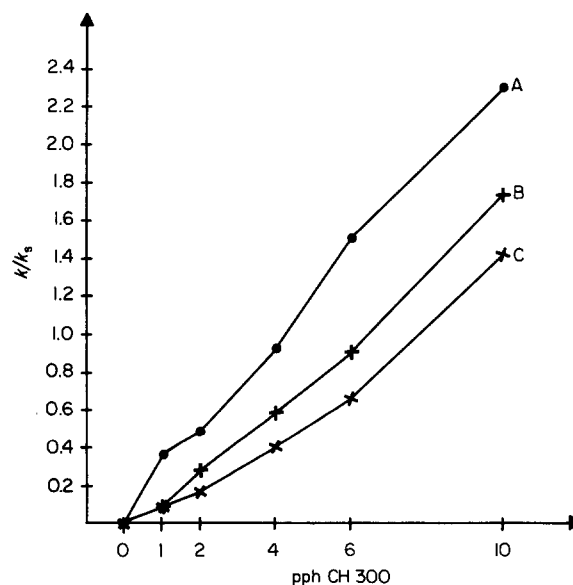


Figure 2 Reduced quotient (k/k_s) for PVC-samples vs. amount of added CH 300. Curve A: Samples mixed at 110°C for 20 min; Curve B: Samples mixed at 110°C for 20 min and thereafter rolled at 170°C for 5 min; Curve C: Samples mixed at 110°C for 20 min and thereafter rolled at 170°C for 15 min

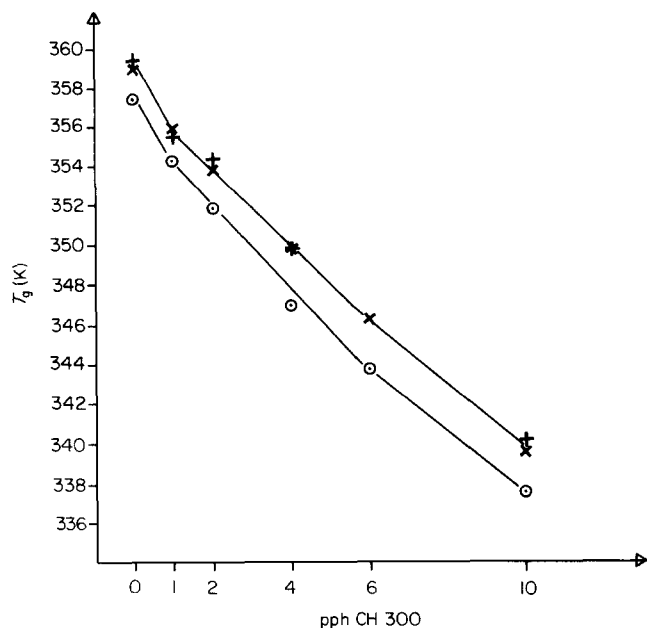


Figure 3 Glass transition temperatures for PVC-samples vs. amount of added CH 300. (—○—) Samples mixed at 110°C for 20 min; (—+—) Samples mixed at 110°C for 20 min and thereafter rolled at 170°C for 5 min; (—×—) Samples mixed at 110°C for 20 min and thereafter rolled at 170°C for 15 min

samples. The assumption of a lower degree of entanglement in powdered samples compared with the corresponding rolled products thus seems to be necessary in order to explain the results obtained here.

Since the intensity of the narrow line of the n.m.r. spectrum increases and the T_g of PVC decreases continuously with further addition of CH 300, we assume that equilibrium conditions are not attained. However, the situation may also be that the phase relations cannot be described by simply assuming that the systems are formed by a liquid phase of pure and unaffected co-stabilizer and by a PVC phase to some degree swollen by the additive. These questions will be the subject of further studies.

Corresponding investigations have also been performed for an impact modified PVC-EVA (polyethylene vinylacetate copolymer with 45 wt% VAc) graft polymer with 8% EVA. This graft polymerized product is produced by Kema Nord AB, Stenungsund, Sweden, and shows relatively constant phase conditions between PVC and EVA. The results from these measurements have been reported earlier where we have shown that an increase of added co-stabilizer increases the thermal mobility of the EVA-phase⁴. We can also observe a decrease of the glass transition temperature of the PVC-phase with an increased amount of CH 300. These measurements are, however, not very informative since the T_g of the EVA-polymer occurs over a wide temperature interval which makes it difficult to draw a correct pre-transition base-line curve with sufficient precision.

The observed partial solubility of CH 300 in rigid PVC seems to be a drawback from the technical applications point of view. This condition may imply a lower efficiency of the product regarding its function as a co-stabilizer. It may also be feared that problems due to migration could be severe for a product which is not completely included in the polymer-matrix.

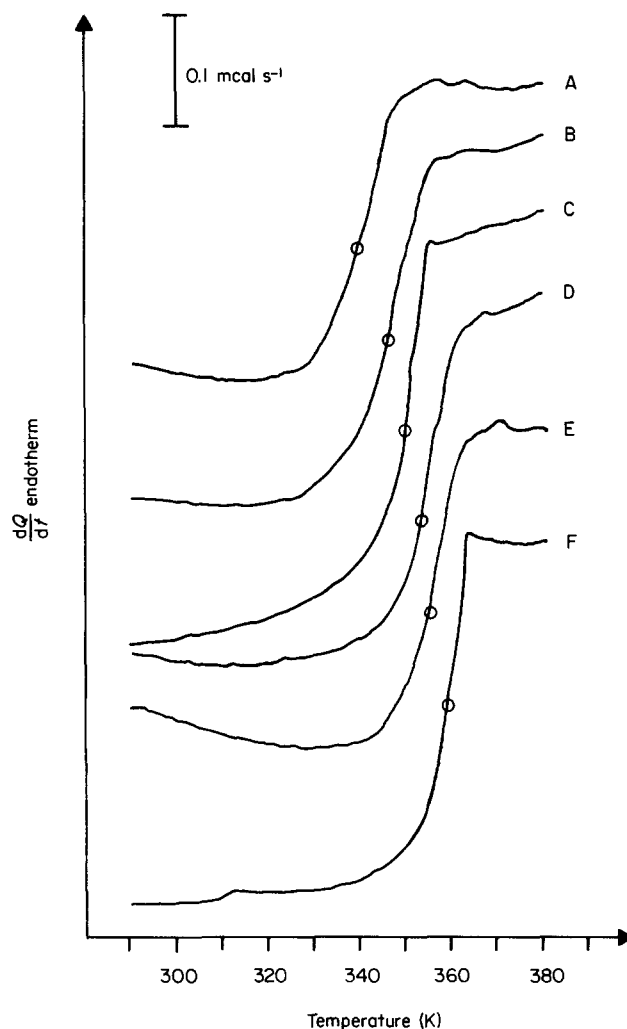


Figure 4 Typical d.s.c. thermograms for PVC samples containing different amounts of CH 300. The present curves represent PVC with different amounts of CH 300 mixed at 110°C for 20 min and thereafter rolled at 170°C for 5 min. The circles represent the estimated T_g 's. Curve A: 10 pph; curve B: 6 pph; curve C: 4 pph; curve D: 2 pph; curve E: 1 pph; curve F: 0 pph

The techniques detailed here show the ease of using wide-line n.m.r. and d.s.c. for investigating solubility conditions. It is our intention to extend these techniques so that finer details may be measured.

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