

# Solution Process of Suspension Poly(Vinyl Chloride) in Cyclohexanone by Means of a Viscometer

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## SYNOPSIS

To study the structure of grains of suspension poly(vinyl chloride) (PVC), the authors applied a capillary viscometer for cyclic measurements of viscosity of the PVC-cyclohexanone solution during dissolution of the polymer. Final concentration of the solution was 0.5–1.0 g/100 cm<sup>3</sup> and the measurements were made at temperatures of 313, 333, 353, and 373 K. It was found that at 353 K, a temperature close to the glass transition temperature of PVC, the curve describing changes of viscosity vs. the dissolution time has a pronounced maximum. It follows from a preliminary analysis of the obtained results that this maximum corresponds to the viscosity of a PVC solution in which average apparent mass is many times larger than true average molecular mass of the studied sample. It means that into the solution enter single chains and some formations, called microdomains in the literature, that are composed of tens of macromolecules. The microdomains disintegrate later to single macromolecules.

## INTRODUCTION

Grain morphology is one of the most important parameters of poly(vinyl chloride) (PVC) both in respect of processing characteristics and the performance of manufactured products.<sup>1</sup> Despite the availability of many experimental techniques applicable to the studies of porosity and morphology on the macro-, micro-, and submicro scales, a complete explanation is still missing concerning the existence and stability of submicroscopic formations that do not change during processing of PVC<sup>2</sup> and that can significantly influence the ultimate characteristics of fabricated articles.

The morphology of the grain is developed during the polymerisation process of vinyl chloride. Authors of the published work studied the morphology of samples of suspension PVC grains by attempting to reverse the process of grain formation. To this end, they studied the solution process of raw PVC grains in cyclohexanone, periodically measuring the solution viscosity while increasing concentration until the whole polymer was dissolved.

## EXPERIMENTAL

Samples of commercial polymers of suspension PVC from both Nitrogen Works Tarnów (tarvinyl 64) and Nitrogen Works Włocławek (polanvil 67) were used in the studies. The polymers had similar mass distribution curves as estimated by the gel permeation method.<sup>3</sup> Viscosity measurements were made by means of an automatic Ubbelohde capillary viscometer (Fica model 52000) equipped with a capillary with an inner diameter of 0.5 mm. Cyclohexanone from the Nitrogen Works Tarnów was distilled and for further analyses only the fraction boiling at 428–429 K was taken. The experiments were made as follows: Initially, 5 cm<sup>3</sup> of the solvent was introduced into the container of the thermostated viscometer. Using a glass funnel, a weighed amount of the polymer was poured into the container. Finally, the funnel was rinsed with a second 5 cm<sup>3</sup> portion of the solvent. The undissolved polymer settled and remained at the bottom of the container under a layer of solution. The solution was then forced into the capillary at regular intervals and its flow times, between fixed levels in the capillary, were measured. Identical control measurement was also made with the pure solvent. Measurements were made at temperatures of 313, 333,

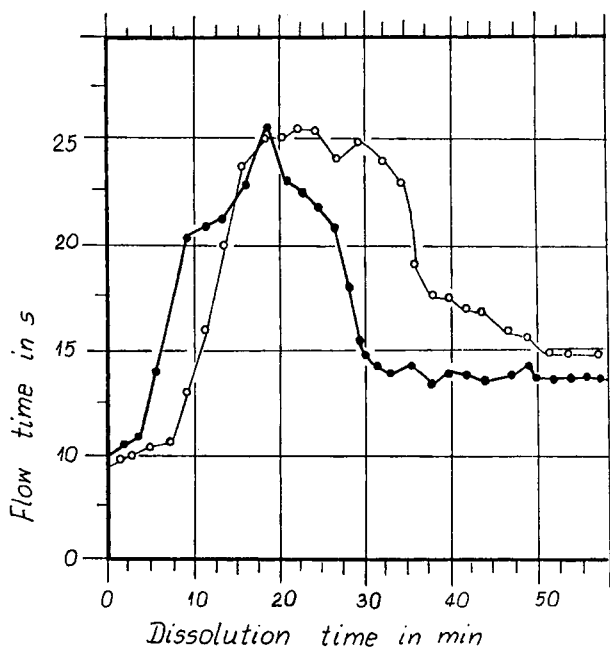
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353, and 373 K. The time intervals at which the viscosity was measured were adjusted to suit the different rates of polymer dissolution at the four temperatures. The measurements were continued until the flow times became constant. Depending on the amount of polymer used, the final solution concentrations were equal either to 0.5 or 1.0 g/100 cm<sup>3</sup>.

## RESULTS AND DISCUSSION

As anticipated,<sup>4</sup> interesting results were obtained only when the viscosity measurements were made at 353 K, i.e., at a temperature close to the glass transition temperature, which in the case of PVC is approximately 357 K. Changes in solution viscosity as a function of polymer dissolution time are presented in Figure 1. Similar curves were obtained for both polymer samples studied, i.e., curves having strong maxima at which values of the viscosity are 2.5 times larger than viscosities of the final solution. In the case of polanvil 67, the reduction in viscosity from its maximum value is slower.

The solution process of a high molecular mass polymer in a solvent comprises at least three stages. During the first stage, the polymer is introduced into the solvent and initially no distinct signs of any interactions between the two can be observed. Subsequently, solvent molecules penetrate the polymer,



**Figure 1** Dependence of viscometric flow times of PVC-cyclohexanone solutions at 353 K on the time of dissolution. ●, tarvinyl 64; ○, polanvil 67.

causing it to swell. At this stage, only few macromolecules enter into solution due to their small diffusion coefficients. Finally, the swollen polymer particles disintegrate and single macromolecules diffuse into the solvent, forming a true solution.

In a typical solution process of a polymer, one might expect a constant increase in the solution concentration until the polymer is completely dissolved. Such a phenomenon would not result in a maximum on a plot of viscosity against time of dissolution. To explain the appearance of maxima on curves in Figure 1, the following Huggins and Mark-Houwink equations were applied

$$\frac{1}{c} \frac{\eta - \eta_0}{\eta_0} = \frac{1}{c} \frac{t - t_0}{t_0} = [\eta] + k'[\eta]^2 c \quad (1)$$

and

$$[\eta] = KM^a, \quad (2)$$

where  $\eta$  and  $\eta_0$  are viscosities of solution and of pure solvent while  $t$  and  $t_0$  are flow times in the viscometer capillary of solution and of pure solvent, respectively,  $c$  is concentration,  $[\eta]$  the limiting viscosity number,  $k'$  the Huggins' constant,  $M$  is molecular mass, and  $K$  and  $a$  are parameters.

From eqs. (1) and (2), the following relation can be obtained

$$t/t_0 = 1 + KM^a c + k'(KM^a)^2 c^2. \quad (3)$$

It follows from the last equation that the presence of maxima on curves in Figure 1 is due only to the value of mass  $M$ , which should be many times larger than the average molecular mass of the polymer being dissolved. To estimate the average mass of the formations that exist in solution at the moment of appearance of the maximum value of its viscosity, eq. (3) was used in which the last term was neglected. This omission causes an error of the order of 20% (see Appendix). Rearrangement of the simplified eq. (3) gives:

$$M = \left( \frac{1}{cK} \frac{t - t_0}{t_0} \right)^{1/a} \quad (4)$$

Equation (4) may be written separately for the maximum viscosity in Figure 1 utilizing the quantities  $M_{\max}$ ,  $t_{\max}$ , and  $c_{\max}$ , and for the final, steady viscosity utilizing the viscosity average molecular mass  $M_v$ ,  $t$ , and  $c$ . Rearranging these two versions of eq. (4), one gets the following relation:

$$\frac{M_{\max}}{M_v} = \left( \frac{c}{c_{\max}} \frac{t_{\max} - t_0}{t - t_0} \right)^{1/a} \quad (5)$$

Using eq. (5), one can estimate how many times larger the average mass of the formations existing in the solution with highest viscosity should be compared to the  $M_v$  value of the polymer. As already mentioned, the value of  $c_{\max}$  was approximately equal to 0.5  $c$ . Numerical values of the flow times  $t_0$ ,  $t_{\max}$ , and  $t$  may be taken from Figure 1 and are equal to 10, 50, and 20 s, respectively. Parameter  $a$  has for the system PVC-cyclohexanone, at 333 K, a value of 0.801. Substituting all above-mentioned numerical values into eq. (5), one gets the following quantity:

$$\frac{M_{\max}}{M_v} = \left( \frac{c}{0.5c} \frac{50 - 10}{20 - 10} \right)^{1/0.8} = 13.5. \quad (6)$$

The last result means that in the dissolution process of PVC in cyclohexanone, at a temperature close to the glass transition temperature of the polymer, in addition to single polymer chains, formations composed of tens of macromolecules also enter into the solution. These are linked for some time until the diffusing solvent molecules disintegrate them. This observation could be considered evidence of existence in the suspension PVC of ordered regions, bound together more strongly by their intermolecular interactions than the surrounding regions of unordered chains. At the PVC glass transition temperature, the atactic regions of the polymer are more mobile, enabling easier penetration of the polymer by solvent molecules. It may be assumed that single macromolecules enter into the solution from the unordered regions of the polymer grains, while the ordered formations enter as a whole. The resultant effect of such a dissolution process manifests itself in a very significant increase in solution viscosity at the initial stage of polymer dissolution.

Based on results of microscopic studies, it was stated in the literature<sup>1,2,6</sup> that formations (approximately 10 nm large) with an ordered structure, composed probably of 50 polymer chains, exist within the PVC grains. To simplify considerations further, the assumption is made that the weight-average molecular mass  $M_w$  of the studied polymer is approximately equal to  $M_v$ . Thus, the viscosity of the PVC solution is proportional to  $M_w$ . At the moment when maximum value of the solution viscosity is achieved (Fig. 1), two different components may be found in the solution, i.e., single chains with an average molecular mass  $M_w$  and formations of, say,

50 chains whose average mass would be  $50M_w$ . Thus,  $M_w$  of the polymer system composed of these two species— $M_{w,s}$ , being equal to  $13.5M_w$  [eq. (6)]—may be calculated from the following relation:

$$M_{w,s} = w_1M_w + w_250M_w, \quad (7)$$

where  $w_1$  and  $w_2 = 1 - w_1$  are weight fractions of the single chains and multiple chain formations, respectively. Substituting corresponding numerical values into eq. (7), one can calculate that  $w_1 = 0.75$  and  $w_2 = 0.25$ , which means that the ordered formations constitute 25% w/w of the solution polymer concentration at its maximum viscosity. Considering now the corresponding numbers of single chains and multichain formations, one can start from the basic dependence of the number fraction  $n$  on the weight fraction  $w$ , namely:

$$w = nM, \quad (8)$$

where  $M$  is the molecular mass.

Hence, the corresponding relations for single chains and multichain formations are as follows:

$$w_1 = n_1M_w \quad (9)$$

and

$$w_2 = n_250M_w. \quad (10)$$

The number fraction ratio  $n_1/n_2$  may be obtained by dividing the above two equations by sides and rearranging, with the following result:

$$\frac{n_1}{n_2} = \frac{w_150M_w}{w_2M_w} = \frac{50w_1}{w_2} = \frac{150}{1}. \quad (11)$$

The last result means that in the studied cyclohexanone solution of suspension PVC there exists at the maximum value of its viscosity 1 multichain formation (assumed here to contain 50 ordered macromolecules) for every 150 single chains.

## CONCLUSIONS

Applying the results of viscometric studies of the dissolution process of samples of suspension PVC in cyclohexanone at 353 K, i.e., at a temperature close to the glass transition temperature of the polymer, the existence in this polymer of formations composed of tens of macromolecules, with consid-

erable intermolecular interactions, was confirmed, testifying to the ordered structure of these formations.

The studies will be continued to establish, amongst other things, if the ordered formations in PVC samples obtained in polymerisation processes with different types of surfactants used exist universally and whether there are any differences between these formations in polymers coming from different PVC producers.

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## APPENDIX

Neglecting the last term of eq. (3) means that in eq. (1), whose right-hand side may be written as  $[\eta](1 + k'[\eta]c)$ , the term  $k'[\eta]c$  is omitted in comparison with unity. For the system studied in this work, the calculated value of  $[\eta]$  according to eq. (2) is  $154 \text{ cm}^3/\text{g}$ . In the calculations of  $[\eta]$ , the literature values<sup>7</sup> of the parameters  $K = 1.586 \cdot 10^{-2} \text{ cm}^3/\text{g}$  and  $a = 0.801$  at 333 K and of the  $M_w$  value of the studied samples being approximately equal to  $95,000^3$  were taken. The concentration  $c$ , corresponding to maxima of curves in Figure 1, was measured experimentally and was approximately equal to  $0.005 \text{ g/cm}^3$ , i.e., to half the value of the final concentration.

To estimate value of the Huggins' constant  $k'$ , the approximate relation  $k' = 1.1 - a$ , cited by van Krevelen,<sup>8</sup> was applied, where  $a$  is the exponent in eq. (2). Thus,  $k' = 1.1 - 0.8 = 0.3$ .

Summing up, the term  $k'[\eta]c$  has, here, the value of 0.23. Thus, by neglecting this term in further analysis of eq. (3), an error of the order of 20% is introduced.

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