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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Radiation-Induced Heterophase Polymerization of Vinyl Chloride: Influence of Additives on the Particle Morphology

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**To cite this Article** Carena, M. , Palma, G. , Talamini, G. and Tavan, M.(1977) 'Radiation-Induced Heterophase Polymerization of Vinyl Chloride: Influence of Additives on the Particle Morphology', *Journal of Macromolecular Science, Part A*, 11: 7, 1235 – 1248

**To link to this Article:** DOI: 10.1080/00222337708061323

**URL:** <http://dx.doi.org/10.1080/00222337708061323>

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## **Radiation-Induced Heterophase Polymerization of Vinyl Chloride: Influence of Additives on the Particle Morphology**

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### **ABSTRACT**

Investigations were carried out on the particle morphology of poly(vinyl chloride) obtained in quiescent conditions in the early stages of radiation-induced bulk polymerization at 50° C and 70° C of vinyl chloride with methanol added in small

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percentages. In the presence of the additive, small-sized particles remaining in a homogeneous dispersed state in the monomer were produced, rather than the very large particles undergoing a rapid sedimentation which would be formed in the polymerization of pure vinyl chloride. An increase in the particle size was observed to take place to a smaller extent with decreasing percentage of methanol and to a larger extent with decreasing dose rate. The increase in the particle size was accompanied, and considerably magnified, by a transition of the particle shape from a smooth spherical one to that of a composite unit originating from a previous agglomeration of smaller particles, when the polymerization temperature of 50°C was involved. Conversely, at 70°C no transition was observed, which was interpreted as the result of a higher plasticization level of the polymer particles favoring to a larger extent a "coalescence" process of the agglomerated units.

## INTRODUCTION

In a previous work [1] the particle morphology of the polymer precipitated during the course of the radiation-induced bulk polymerization of vinyl chloride (VC) in quiescent conditions was examined over a wide temperature range. The data were discussed on the basis of previous findings [2-4] showing the polymerization kinetic patterns to be widely dependent on the temperature and indicating at all the temperatures investigated the polymer phase to be the prevalent locus of polymerization from a very early stage onwards.

The polymer particle formation and growth appeared to be interpretable by a nucleation model similar to that proposed by Fitch et al. [5, 6] for emulsion systems. Immediately after the beginning of polymerization, there is formation of primary particles due to the precipitation of single macromolecules or long macroradicals which grow rapidly in size by sweeping up growing radicals from the liquid monomer phase. New primary particles are formed by those radicals reaching precipitation size before being captured, and whose number decreases with conversion. Simultaneously, the polymer particles undergo a process of flocculation, by which agglomerates of comparatively large size are produced at very low conversions.

Regarding the flocculation process, two different behaviors could be observed, depending on the temperature. At low temperatures, the flocculation proceeds only to a limited extent and ceases when

the agglomerates are of small size and, hence, susceptible to remaining in a state of homogeneous dispersion. These agglomerates, which for the sake of clarity are denoted macroglobules while the constituent particles are denoted microglobules, remain constant in number and increase linearly in size with conversion from the end of flocculation to the point of disappearance of the liquid monomer phase. During this period there is still creation, although at a decreasing rate, of new primary particles; these do not increase the number of macroglobules but are all accreted in the form of small-sized microglobules by the existing macroglobules. The homogeneous dispersions of the macroglobules in the liquid monomer are not truly stable. Actually, they are to be considered to be due to a drastic reduction in the flocculation rate with increasing particle volume, such as to prevent further flocculation within the time of the experiment.

When temperatures of 20°C and above are concerned, the state of homogeneous dispersion is no longer retained by the polymerizing systems beyond the very early stages (less than 1% conversion). At these temperatures the flocculation has a higher rate and proceeds to a point at which large flocs are formed. Accordingly, the polymer gather rapidly to the bottom of the reaction container, where the particles become all cemented together.

The flocculation rate is decreased, and, hence, the homogeneous dispersions already encountered at low temperatures are obtained by polymerizing VC in the presence of certain additives. It is relevant that these additives include also some common initiators, which might explain the discrepancies with previous authors [7, 8] who reported a constant number of discrete particles increasing in size with conversion for the bulk VC polymerization.

The form of macroglobules obtained in the polymerization of VC with additives changes from that found at the low temperatures to that of perfectly spherical particles exhibiting no microglobule structure as the polymerization temperature rises from 20°C to 70°C. A behavior similar to that of emulsion liquid droplets was invoked for the highly plasticized polymer particles at 70°C, which thus permit a "coalescence" process to take place in the agglomerates produced by flocculation.

At 70°C macroglobules of spherical shape were generally obtained, but at the intermediate temperature of 50°C the macroglobules were either of this type or with the above composite structure, depending on the polymerization conditions.

Since these facts have been the object of only few observations in a previous work [1], more systematic investigations have been thought to be desirable. They were confined to the initial stages

of polymerization up to about 10% conversion. Methanol was used as stabilizing additive.

## EXPERIMENTAL

### Material

VC provided by Montedison S. p. A. contained trace amounts of chloroalkanes, alkenes, and butadiene.

Methanol (Rudipont RGC) was fractionally distilled immediately prior to use.

### Procedure

Purification of VC through radiation-induced prepolymerization and its degassing by freezing-thawing cycles have been previously described [1-3]. Thick-walled Pyrex glass vials were charged each with 3-4 g monomer and sealed off by flame under vacuum. In the case of runs with methanol, the methanol was introduced in the vials in the prescribed amount before the monomer.

The polymerizations were induced by  $\gamma$ -rays from a cobalt-60 source at various dose rates, as previously described [1, 2]. The determinations of the polymerization conversion were made gravimetrically. The transmission electron microscopy (TEM) analysis was carried out as in the previous work [1]. At completion of the polymerization, each vial was placed in an excess of methanol at  $-30^{\circ}\text{C}$  and broken by stirring. The resulting dispersions of PVC particles in methanol were sprayed onto Formvar films supported on 200-mesh copper screens. These preparations were employed to obtain the electron microphotographs of the polymer particles, by use of a Philips E-M-200 type PW 6000 transmission electron microscope.

## RESULTS AND DISCUSSION

As reported in the previous work [1], the radiation-induced polymerization of pure VC at  $50^{\circ}\text{C}$  and  $70^{\circ}\text{C}$  gave rise to systems in which almost all the polymer was on the bottom of the vial and only a small fraction remained dispersed in the supernatant liquid monomer. While the former polymer could by no means be dispersed,

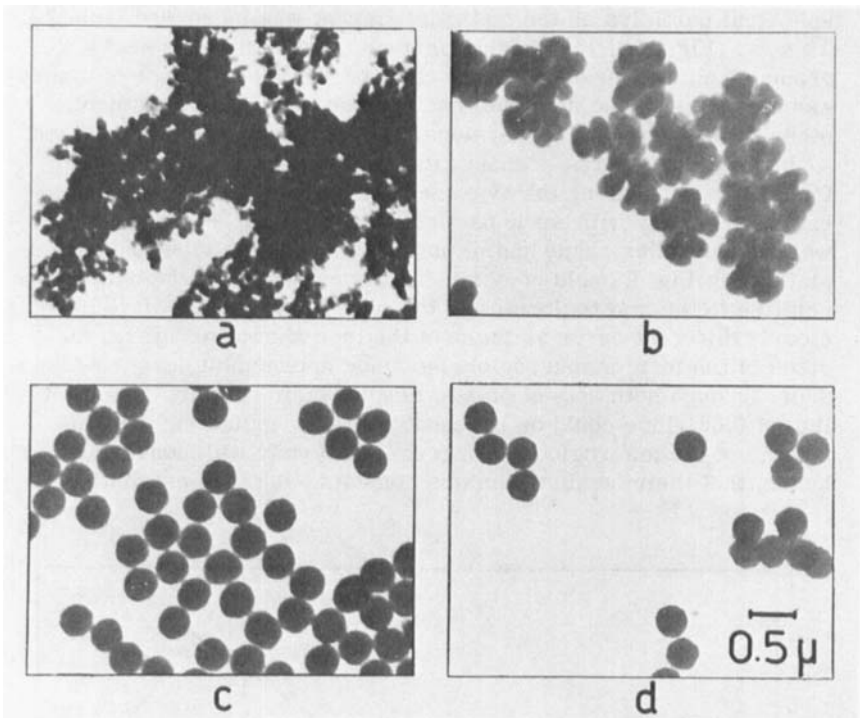


FIG. 1. Electron micrographs of PVC particles obtained by polymerization of VC carried out up to 1% conversion at 44 rad/sec and 50°C; (a) no additive, (b) 2% w/w methanol, (c) 3% w/w methanol; (d) at 16.4 rad/sec and 70°C, 2% w/w methanol.

the dispersed polymer was found to consist of giant agglomerates, an example of which is shown in Fig. 1a. Understandably enough, no conversion dependence was found for such agglomerates.

At both temperatures the addition of small percentages of methanol (less than 1% w/w) to VC made the polymerizing systems remain in the dispersed state, with latexlike appearance, for the whole range of conversions investigated.

With polymerization at 50°C the shape and size of the macroglobules were found to change with increasing percentage of methanol, at variance with the case of the polymerization at 70°C. In particular, in the polymerization at 44 rad/sec at 50°C the macroglobules changed from the composite structure type to smooth

spherical particles as the methanol amount was increased from 2 to 3% w/w, (Figs. 1b, 1c). Higher methanol contents, such as 4% w/w, produced no further appreciable change. This dependence of macroglobule shape on the methanol content was confirmed by a number of other runs at various conversions; very few exceptions were noted.

In addition to particle shape, the macroglobule size was also found to vary. Taking the average particle diameters (which was rather arbitrary with such particles as those in Fig. 1b, which were of irregular shape and of not narrow size distribution), the plots as in Fig. 2 could be obtained. As can be seen, the data points relative to the macroglobules of the type shown in Fig. 1b lie on a clearly different curve as those of the type shown in Fig. 1c, the sizes of the former macroglobules being appreciably larger. Moreover, through both sets of points, despite their scatter, a straight line of 0.33 slope could be reasonably drawn, indicating that the volume of the macroglobules increases linearly with conversion and, hence, that their number remains constant. A rough estimation of

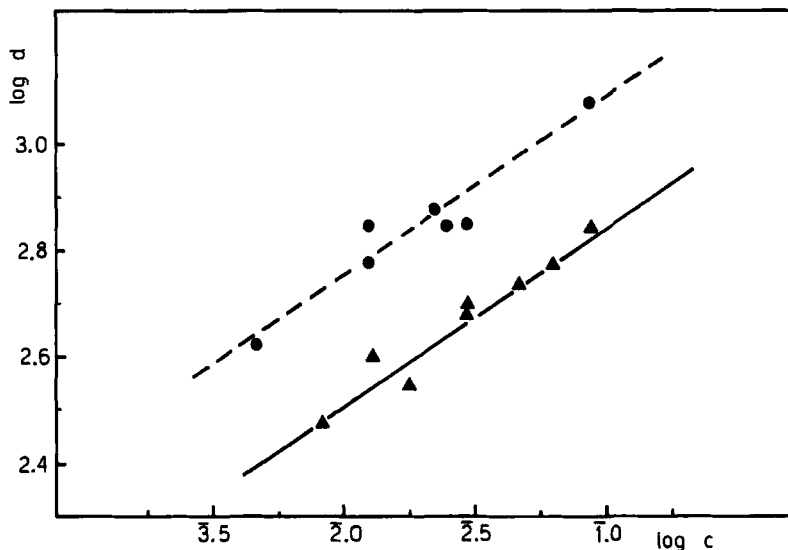


FIG. 2. Dependence of macroglobule diameter (nm) on fractional conversion in polymerization of VC at 50°C and 44 rad/sec in the presence of methanol: (●) 2% w/w; (▲) 3% w/w. The two straight lines are drawn with a 0.33 slope.

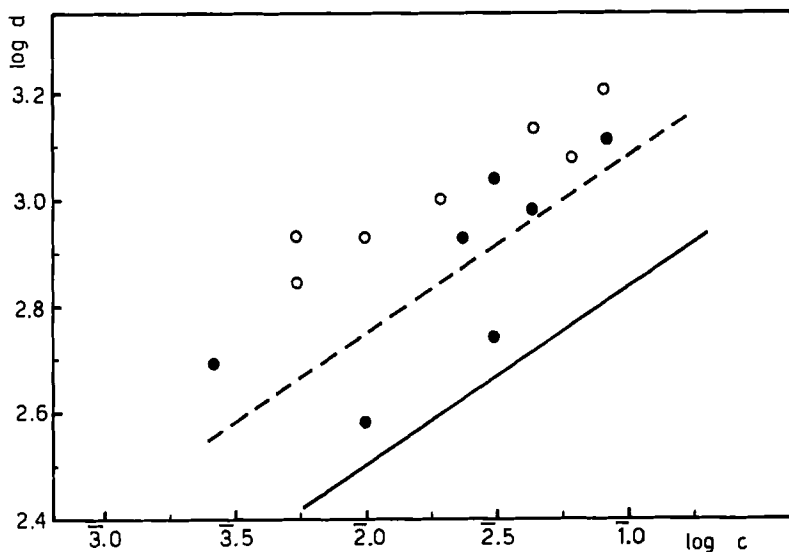


FIG. 3. Dependence of macroglobule diameter (nm) on fractional conversion in polymerization of VC with 3% w/w methanol at 50°C and dose rates of: (●) 2.86 rad/sec; (○) 0.37 rad/sec. For comparison the two lines of Fig. 2 are also included.

this constant number gave the values of  $4 \times 10^{11}$  and  $7 \times 10^{10}$ /g monomer at the start for the spherical macroglobules and the composite ones, respectively. The former value lies rather near to those found in the chemically initiated polymerization at 50°C by Cotman et al. [7] for much lower initiation rate and Kuchanov et al. [8] for an initiation rate similar to the present one.

Another factor influencing the particle morphology was found to be the polymerization initiation rate. In fact, polymerization runs of VC with 3% w/w methanol, carried out at the two lower dose rates of 2.86 and 0.37 rad/sec, gave mostly macroglobules of composite structure and of large size. The latter, as shown by Fig. 3, appear in general to exceed in size the macroglobules of the same type formed in polymerization with 2% w/w methanol at 44 rad/sec. Despite the scatter of the data points, Fig. 3 shows that there is a certain initiation rate dependence of the number of the macroglobules. This can be roughly expressed as:

$$N \propto R_i^{0.25} \quad (1)$$



where  $N$  is the number of macroglobules per unit volume and  $R_i$  is the initiation rate.

Since a similar dependence was derived for the macroglobules obtained in the polymerization of pure VC at  $-10^\circ\text{C}$  [1], the same assumption that the number of the macroglobules is considerably affected by the flocculation process can be made here.

In these considerations, the two data points for a dose rate of 2.86 rad/sec, which lie in a considerably lower region of the diagram of Fig. 3, were not included. Since in these cases macroglobules of spherical shape were involved, their approaching the line representing the macroglobules of the same type for polymerization at 44 rad/sec is not surprising. These anomalous findings and those corresponding to the formation of macroglobules of spherical shape in the polymerization of VC with 2% w/w methanol at 44 rad/sec, of which some mention was already given above, seem to point to the influence of other, not easily controllable, factors.

All the results reported so far can be explained on the basis of the previous assumptions [1]. The flocculation proceeds virtually stepwise with a flocculation rate constant which decreases at every step due to the increase in volume of the flocculating particles. Eventually, a particle size is attained such as to result in a very strong reduction of this rate constant with the consequence that the flocculation practically ceases. If this particle size is small enough, homogeneous dispersions are obtained. Although this is not the case for the polymerization temperature above  $20^\circ\text{C}$ , when pure VC is concerned, it becomes so in the presence of methanol, which causes the flocculation rate constant to decrease substantially.

Further, if the logical assumption is made that the larger the amount of methanol, the greater is its stabilizing effect, the resulting decrease in the macroglobule size with increasing methanol percentage can be readily accounted for, as the stepwise flocculation process would stop at an earlier step and thus leave more macroglobules in the system. Regarding the fact that in this case the macroglobules also assume a spherical shape, the process of "coalescence" can be considered to follow flocculation very rapidly when small flocculating particles are involved [1]. As the flocculation proceeds and larger particles are formed, this "coalescence" takes place only partially, and macroglobules of composite structure like those in Fig. 1b are obtained.

Such a transition in the macroglobule shape, moreover, might to a certain extent account for the fact that, when it occurs, there occurs also a most important increase in the number of macroglobules with increasing methanol percentage, if a lower flocculation rate [9] is considered to prevail for spherical particles with respect to the particles of equal size but of different shape.

The change in particle morphology produced at a fixed methanol amount as a result of changes in the initiation rate appears to be in line with a logical expectation. Since a larger rate of free radical generation should result in a larger number of primary particles in the system at the start, it is reasonable to expect also a larger number of agglomerates in the system at the end of the flocculation process.

Another line of reasoning, similar to that adopted by Bort et al. [10] for results of the same kind, is also possible. In the flocculation process, considered to proceed stepwise as a rough approximation [1], a sufficiently rapid increase in volume of the particles produced at a certain step should result in a substantially reduced flocculation rate before the subsequent step. Thus, a larger initiation rate corresponding to a more rapid increase in volume of all the particles in the system will make the flocculation process cease at an earlier step, as in the case above of a higher level stabilization with all the consequences already discussed.

In this picture one can accommodate with some plausibility the above mentioned anomalous findings, which seem to refer to conditions either of a higher stabilization level than that corresponding to the amount of alcohol introduced or of a higher polymerization rate than that corresponding to the dose rate applied. It is necessary to assume only that trace amounts of impurities acting as retarders are normally present in the system. Even if their consumption occurs in the very early stages and, hence, with negligible consequences for the kinetic curve as a whole, nevertheless a considerable reduction in the polymerization rate might well be produced just in those stages in which the flocculation process takes place. It should be borne in mind that the formation of the macroglobules appears to be completed below 0.2% conversion. Thus, such anomalous results could be considered to arise from especially favorable conditions of purity in the systems. Moreover, the reverse can be predicted as well, for conditions more unfavorable than those normally encountered; indeed, experimental evidence for this has also been found.

A point worth noting in the polymerization at 50°C is that the dependence of particle morphology on the percentage of additive and the dose rate is made much more marked by the occurrence of the macroglobule shape transition. Since for the latter it has been assumed that the flocculating particles undergo a complete "coalescence" process until they are below a certain size and only an incomplete one thereafter, undoubtedly such a critical particle size should be very small at 50°C.

Larger critical particle size values can be predicted for the polymerization at 70°C, where polymer particles more similar in

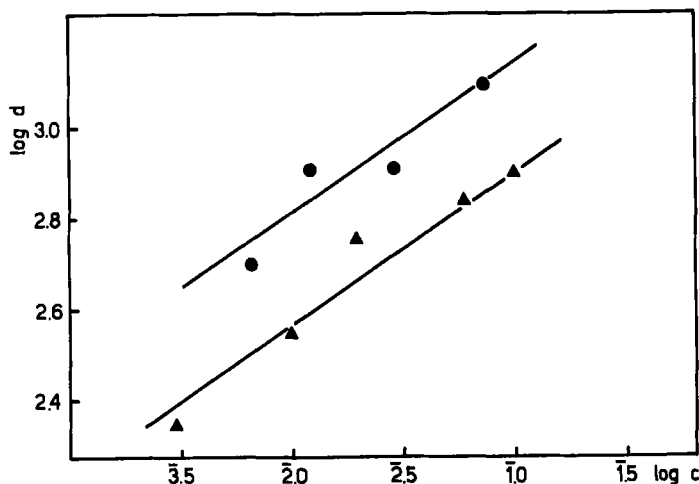


FIG. 4. Dependence of macroglobule diameter (nm) on fractional conversion. Polymerization of VC with 2% w/w methanol at 70°C and dose rates of: (●) 0.37 rad/sec; (▲) 16.4 rad/sec. The two lines are drawn with a 0.33 slope.

behavior to the liquid droplets of emulsion systems are not unexpected. Accordingly, macroglobules of smooth spherical shape and of size little affected by the type and amount of additive have been observed [1]. In order to have a complete view, also the influence of the other parameter has been examined.

Polymerization runs at 70°C with 2% w/w methanol were carried out at a dose rate as low as 0.37 rad/sec. As predicted, the macroglobules were found to exhibit a smooth spherical shape and to be of considerably large size, as shown in Fig. 4. The concentration of macroglobules in monomer is found to be about  $5 \times 10^{10}$  per gram, which is somewhat lower than the value assigned for the case of the macroglobules of composite structure for polymerization at 50°C and 44 rad/sec with 2% w/w methanol.

In this context, it should be borne in mind that these results are not consistent with the view held by Bort et al. [10] on the correlation between the PVC particle morphology and the polymerization parameters. In their polymerization systems, in which the initiator probably acted as a dispersion stabilizer, they observed a progressive decrease in the size of the macroglobule and in the complexity

of its structure with increasing initiator concentration and/or increasing temperature. In their interpretation of the effects of these two parameters, only the resulting increase in the polymerization rate was taken into account by the mechanism cited above, according to which the more rapid the increase of the particle size, the less probable is the occurrence of the flocculation process. On the contrary, the present results show that it is possible to obtain macroglobules of smooth spherical shape at a much lower polymerization rate at 70°C than at 50°C. However, one should consider that the polymerization rate has been established [ 2, 3 ] to depend on the square root of dose rate and to increase insignificantly at a fixed dose rate when the temperature is raised from 50°C to 70°C. Actually, the case is somewhat different if the polymerization rate at the start is involved, but, even then, the increase is not larger than 30%. Consequently, an effect of the temperature increase on the particle morphology other than an increase in polymerization rate should be formulated. Clearly, such an effect can be reasonably envisaged in the increase of plasticization of the polymer particles, favoring the process of coalescence.

Moreover, it is worth noting that these considerations do not support the view [ 10 ] that the macroglobules of smooth spherical shape are formed only under the conditions which entirely prevent the flocculation process from taking place. The same can be said on the account of the rather low number of macroglobules per gram of monomer found in the system polymerized at 70°C with 0.37 rad/sec.

A final point to consider is the value of about  $3 \times 10^{11}$  macroglobules per gram of monomer determined in the polymerization at 70°C with 16.4 rad/sec, the data points of which are also shown in Fig. 4. The dependence of number of macroglobules on dose rate, which can be very roughly calculated from this value and the value at 0.37 rad/sec, is:

$$N \propto R_i^{0.45} \quad (2)$$

It is interesting to note that this dependence is appreciably larger than in the case of the composite macroglobules produced at 50°C, indicating a less important flocculation process at 70°C.

More investigations on the dependence of particle morphology on dose rate, especially on the occurrence of the flocculation process, would be desirable.

An obvious question suggested by the large differences in the PVC particle morphology with changes in the polymerization kinetics is

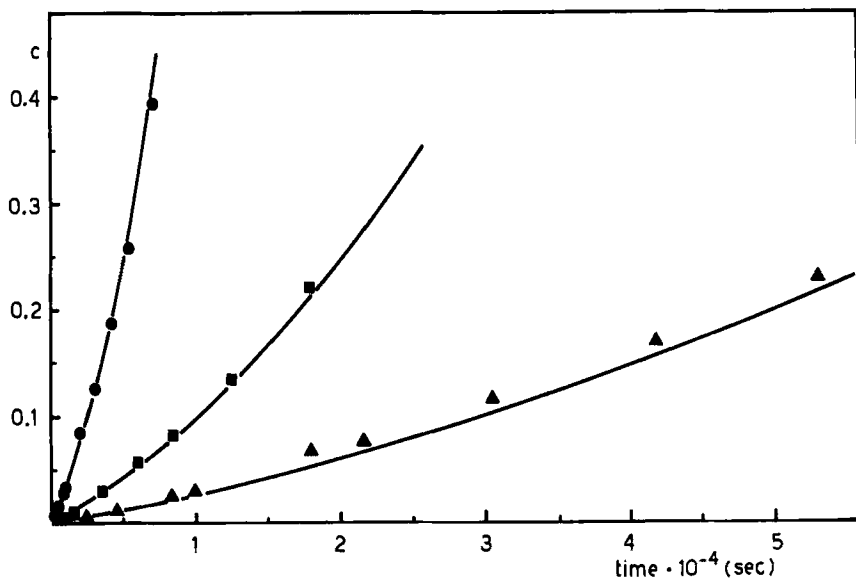


FIG. 5. Fractional polymerization conversion vs. time plots of VC with 3% w/w methanol at 50°C and dose rates of: (●) 44 rad/sec; (■) 2.86 rad/sec; (▲) 0.37 rad/sec. The curves, derived from Tavan et al. [2], represent the corresponding kinetic curves for the polymerization of pure VC.

whether the particle morphology, in turn, has some bearing on the kinetics.

In formulating a kinetic model for the bulk polymerization of VC a great importance has been attached [7, 8, 10-15] to the fact that dispersions of polymer particles are produced. Moreover, changes in the particle morphology and deviations from the state of homogeneous dispersion have been postulated [7, 11, 15] to be of some consequence for the polymerization kinetics. In agreement with this view, an appreciable reduction in the polymerization rate with respect to normal quiescent conditions has been recently observed [2, 4] to occur by a change in the polymer dispersion heterogeneity which was brought up to an extremely high level by performing the polymerization under a centrifugal field.

Conversely, an increase in the polymerization rate should be observed in conditions ensuring a good homogeneity of the polymer

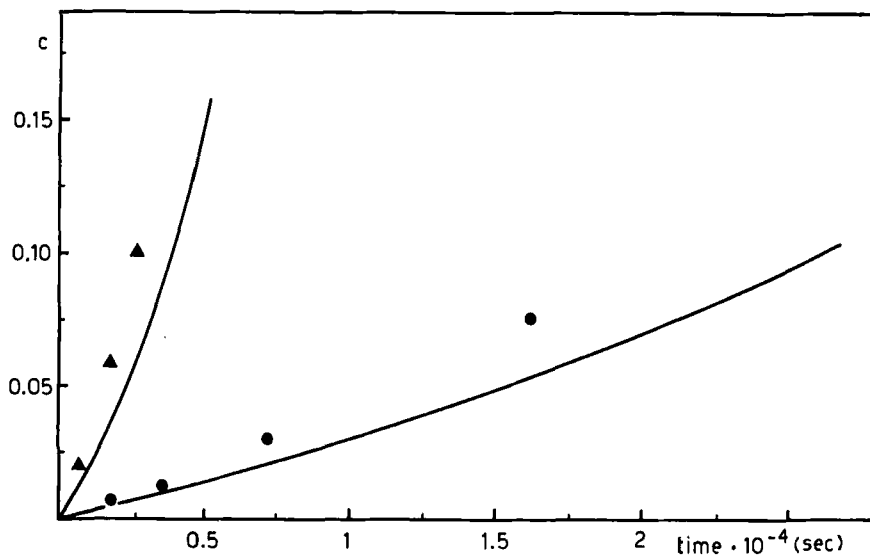


FIG. 6. Fractional polymerization conversion vs. time plots of VC with 3% w/w methanol at 70°C and dose rates of: (▲) 16.4 rad/sec; (●) 0.37 rad/sec. The curves, derived from Tavan et al. [2] represent the corresponding kinetic curves for the polymerization of pure VC.

dispersion in the monomer, as it is the case in the presence of a stabilizing additive.

Conversion determinations for polymerization with methanol at the various dose rates investigated gave the plots shown in Figs. 5 and 6 for 50°C and 70°C, respectively. For comparison, Figs. 5 and 6 also show the corresponding kinetic curves for the polymerization of pure VC as derived from previous studies [2, 3] and in part confirmed by additional runs. As can be seen, the addition of methanol causes the polymerization to proceed slightly faster at 50°C and considerably faster at 70°C. Although this difference in behavior is not easily explained, the results are in agreement with the expectation of a higher polymerization rate with a more homogeneous dispersion in the system. This assertion has been given a sort of further test by carrying out a few runs in the presence of methanol at 70°C in which the vials were subjected to vigorous agitation at intervals during the course of polymerization,

which is known [ 1 ] to give rise to a very rapid sedimentation of the dispersed polymer particles. As expected, this introduction of some heterogeneity in the dispersions gave conversion values lying between the data points and the curves in Fig. 6.

#### ACKNOWLEDGMENTS

The authors are indebted to Mr. S. Franceschini for taking the electron microphotographs and to Professor G. Semerano, Director of the Laboratorio F. R. A. E., C. N. R., for his continued interest in this work.

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