A sensitive method for polymerization control based on ultrasonic measurements

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Ultrasonic measurements during the emulsion polymerization process were recorded on poly(vinyl acetate). In the low conversion region the ultrasonic attenuation provides information on the growth of the particles. In the high conversion region, the ultrasonic velocity is a sensitive tool for observing the polymerization process. On the basis of an empirical formula the conversion may be calculated and this ultrasonic principle is quite appropriate for technological purposes.

(Keywords: ultrasonic studies; polymerization control; particle growth; conversion of polymerization; ultrasonic velocity; acoustic)

INTRODUCTION

Ultrasonic propagation has traditionally been used as a test for high frequency dynamics. Using ultrasonic waves it is possible to sense the molecular structure and motion in liquid polymer systems. The ultrasonic attenuation α is noticeably influenced by the chemical structure and can be associated with conformational changes of elements of the polymer chain of varying size. The ultrasonic velocity usually deals with the structure of the samples being investigated. Therefore, in the case of low molecular hydrocarbon compounds, well defined relations between the velocity c and the chain length or the influence of side or end groups exist[1]. These relations are more complicated in heterogeneous liquid media such as emulsions or polymer solutions.

Usually in simple low molecular liquids the value α/f^2 (f being the measuring frequency) is independent of frequency. When relaxation processes appear in polymer systems the ultrasonic attenuation under observation may be analysed in terms of a distribution of relaxation processes

$$\alpha/f^2 \sim \int_0^\infty \frac{H(\tau)\,\mathrm{d}\tau}{1+(\omega\tau)^2} \tag{1}$$

where $H(\tau)$ is the distribution of the relaxation times τ. In composite media, such as suspensions or emulsions, α is comprises several terms

$$\alpha = \alpha_0 + \sum_i \alpha_i \tag{2}$$

where α_0 is the attenuation of the dispersion medium and α_i are losses due to attenuation mechanisms such as friction, thermal conduction, scattering and relaxation[2].

Sokolov[3] first pointed out the close connections between sonic data and the polymerization process. Later studies on ultrasonic investigations during the polymerization of polystyrene[4] and poly(vinyl chloride)[5,6] have been reported by several workers. In previous studies[5,6] the changes of the rheological properties of the polymerization systems, investigated by attenuation measurements, were discussed, when qualitative conclusions were possible.

The aim of our investigations was to gather quantitative information on the polymerization process based on ultrasonic parameters. Problems which must be solved are: (i) information on the kinetics and the mechanism of polymerization; (ii) data on the conversion.

Our investigations were carried out in the emulsion polymerization of vinyl acetate. Our experience may be transferred to other systems.

EXPERIMENTAL

Methods

Velocities c were measured using a pulse travelling technique at a nominal frequency of 1 MHz and with a precision of 1 part in 10^4. The diameters of the transducers were 2 cm, the distance between both transducers was 7 c, and the pulse width was 1 μs. Attenuation data were obtained at frequencies 2.4 and 4 MHz using a pulse method with variable transducer distances (size of transducers 3 cm). The α measurements were carried out in an external apparatus and the precision of measurements was better than 5%. The polymerization experiments were carried out in a 2 l laboratory reactor. The temperature inside the reactor was measured by a thermistor with an accuracy of 0.2 K. The velocity measurements were carried out inside this reactor.

Samples

The reactor was charged with water, monomer vinylacetate (VAC), initiator potassium persulphate and emulsion stabilizer (ionic tensid or poly(vinyl alcohol) (PVA) with a residual acetate content of 12–14%). The polymerization temperature was 70°C and the pressure 10^5 Pa. The polymerizations were carried out by a number of different methods (solution polymerization, semicontinuous and continuous emulsion polymerization) and to different degrees (low and high conversion).

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RESULTS AND DISCUSSION

Low conversion range

In the case of low conversion, α measurements are very informative as regards the properties of the polymerization system during the particle growth phase. Therefore, we were interested in measuring the attenuation. The basis for our investigations was the variation of α with temperature, which shows a maximum in the MHz range in the case of PVAC[8]. This maximum can be related to the glass transition inside the PVAC particle and the corresponding temperature is denoted by $T_{g,dyn}$, *Figure 1*. In this case the relaxation losses are more prominent than the other losses and they determine the attenuation, as defined by equation (2). The influence of plasticizer on the dynamic glass transition temperature in PVAC dispersions is shown in *Figure 2*. An increase in plasticizer causes a marked decrease in $T_{g,dyn}$. This indicates a change in the molecular mobility[14].

The VAC polymerization starts in an aqueous phase[9]. Oligomers evolve, which then join together and grow as aggregates. This growth of the polymer particles was investigated by attenuation measurements. From about 0.5% volume concentration of the polymer phase it is possible to reproduce the α measurements with satisfactory accuracy. The polymerization was halted at various controlled conversions, and the maximum of the various dispersions was determined. The experimental results are shown in *Figure 3*. In the low conversion range $T_{g,dyn}$ increases with increasing conversion. Loosely packed particles with high mobility exist. Above 3% conversion $T_{g,dyn}$ does not change and corresponds to the value which is equivalent to the final value of the dispersion, and the process of particle growth stops. This final value of $T_{g,dyn}$ may be influenced by the polymerization procedure.

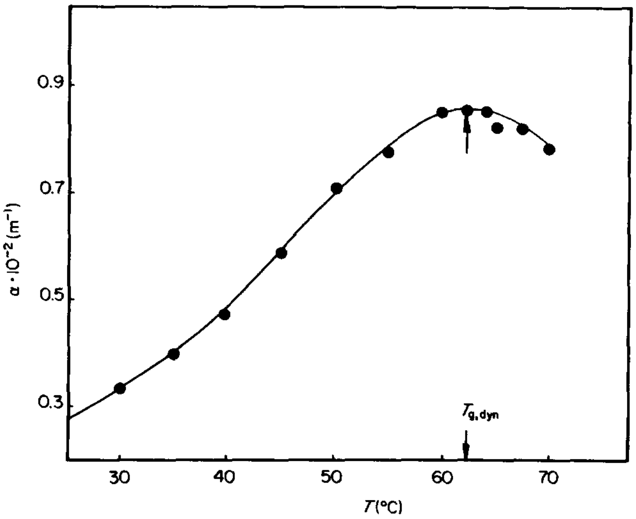

Figure 1 Variation of attenuation α with temperature ($f=2.4$ MHz; PVAC dispersion, $k=5\%$)

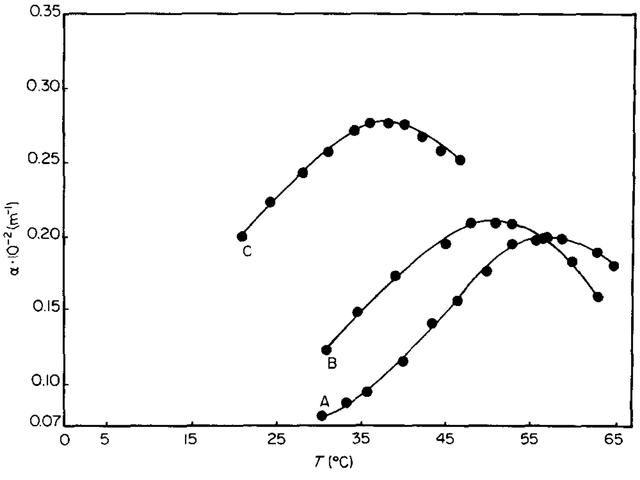

Figure 2 Change in $T_{g,dyn}$ with variation of plasticizer ($f=2$ MHz) A = 1%, B = 5%, C = 30% plasticizer

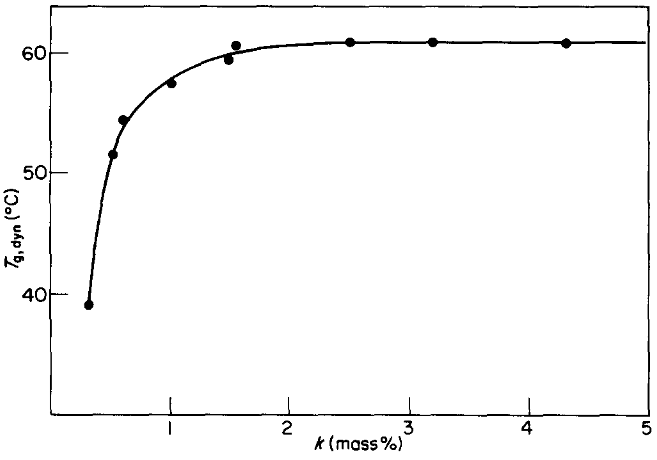

Figure 3 $T_{g,dyn}$ *versus* concentration in the low conversion region

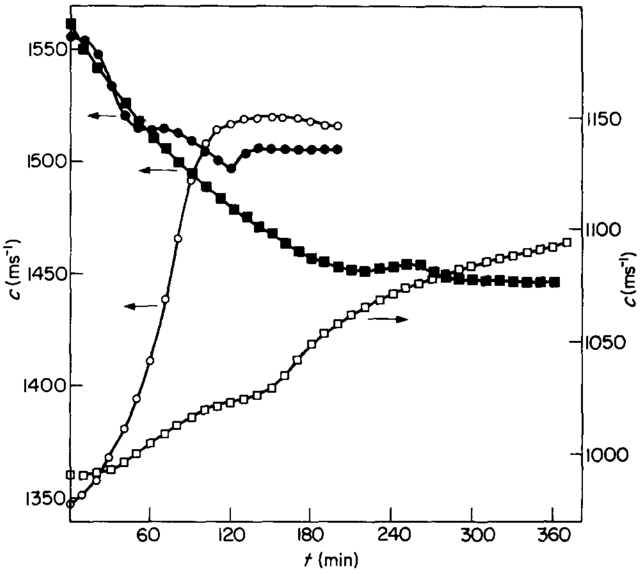

Figure 4 Dependence of c on polymerization time (●, ■ semicontinuous; ○ continuous and □ solution polymerization)

High conversion range

In the case of higher conversion both α and c are sensitive to the actual state of the polymerization. Unfortunately α is strongly influenced by inhomogeneities in the reaction, e.g. the presence of foam can prevent any measurement at all. However, the velocity c of the dispersion is strongly affected by the modification of the different components. Because c can be easily determined with high precision, and because it is relatively simple to construct an automatic measuring system, the ultrasonic velocity technique has proved to be a very useful method for determining the conversion. The following results refer to poly(vinyl acetate).

EXPERIMENTAL RESULTS

Ultrasonic velocity and polymerization process of VAC

The velocity c of the polymerizing system as a function of time is presented in *Figure 4*. The different curves correspond to various types of polymerization. Each polymerization state is characterized by a definite c value. In order to obtain quantitative values of the conversion from velocity measurements, it is necessary to know the sonic properties of all components of the system studied. By choosing a reference medium whose ultrasonic velocity does not change during the process or does vary in any known manner, the change of c due to different components may be described by

$$c = c_0 + \sum_i \left(\frac{\Delta c}{\Delta k}\right)_i k_i \qquad (3)$$

where c_0 is the velocity of the dispersion medium, k_i is the concentration of the i-th component and $(\Delta c/\Delta k)_i$ is the corresponding sound–concentration coefficient. Some examples of the behaviour of different components are given below.

The sonic characteristics of the monomer/water system, depending on the concentration, are illustrated in *Figure 5*. At first the velocity rises and then at a certain concentration the slopes of the curves change. The monomer is solved in water in the area where the slope is positive and is widely dispersed in the area with negative slope. Thus, ultrasonic measurements provide information about the solution limit. Addition of a stabilizer can both change the solution behaviour and influence the degree of compression of the boundary layer[10]. Now it is a complicated problem to investigate the structural changes caused by chemically or physically bonded stabilizer and the influence of dissolved stabilizer on the sound propagation. Experiments were made to try and solve these problems. For example, the change in c as a function of the PVA concentration is displayed in *Figure 6*. The same slope of both curves above 5% indicates that in this concentration region PVA is in a dissolved state in the TiO_2 suspension. A similar behaviour may be assumed in the stabilized PVAC dispersion. To summarize, the acoustic properties of a polymerizing system are rather difficult to qualify, but it may be possible to make quantitative predictions if the influence of the main components are known.

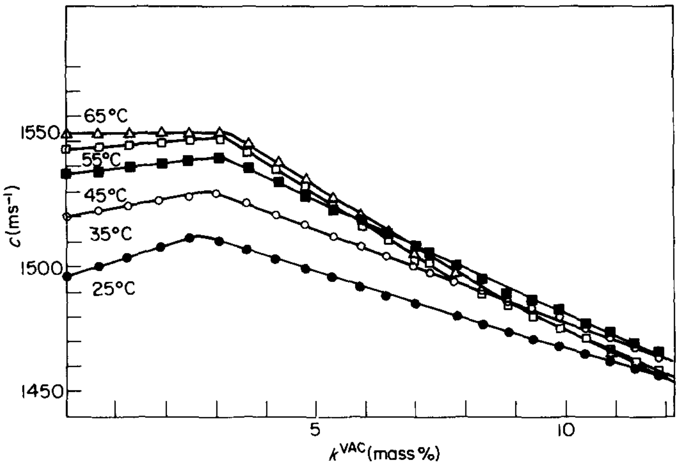

Figure 5 Velocity c *versus* concentration k in the VAC/water system

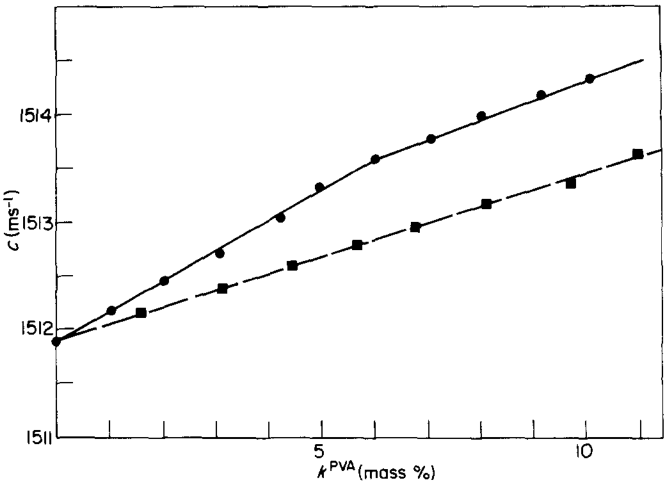

Figure 6 Dependence of c on the PVA content; (●): PVA absorbed on TiO_2; (■): PVA in solution)

Quantitative relations

The first calculations of the velocity c for a heterogeneous liquid system were done by Epstein and Carhart[11]. In later works[2,12] this theory was further developed and applied to suspensions. In all cases complicated relationships between c and the characteristics of the medium such as viscosity, density, particle diameter and compressibility exist. A simplified model for the calculation of c in aqueous polymer dispersion was described in ref. 10. c may be expressed as

$$c^2 = c_0^2 \frac{(1+C)^2}{(1+C\beta'/\beta)(1+C\rho'/\rho)} \qquad (4)$$

where c_0 is the velocity of water, C is the volume part of the disperse phase, β' and β are the compressibilities and ρ', ρ are the densities of the suspended particle and the suspension medium, respectively. An analogous equation was applied for calculations of the compressibility in colloids[13].

All the above mentioned equations cannot easily be applied to the calculations of the velocity during the polymerization process. Based on the equation (2) we were able to develop an empirical relationship between the ultrasonic velocity of the polymerization system and the influence of the different components. For an emulsion polymerization this relation is given by:

$$c = c_0 + \left(\frac{\Delta c}{\Delta k}\right)_{M<L} k_M^L + (k_M^{all} - k_M^L)\left(\frac{\Delta c}{\Delta k}\right)_{M>L}$$
$$+ k_P\left(\frac{\Delta c}{\Delta k}\right)_P + k_I\left(\frac{\Delta c}{\Delta k}\right)_I + k_S\left(\frac{\Delta c}{\Delta k}\right)_S + k_E\left(\frac{\Delta c}{\Delta k}\right)_E \qquad (5)$$

where c_0 is the velocity of the dispersion medium, k_M^L is the limit concentration of the solvated monomer, k_M^{all} is the total used monomer concentration, k_P is the concentration of polymer, k_I is the initiator concentration, k_S is the stabilizer concentration and k_E is the concentration of added electrolytes. $(\Delta c/\Delta k)$ are the corresponding velocity–concentration coefficients. Depending on the type of polymerization, we have:

$k_P + k_M$ constant (continuous polymerization)

or

$k_P + k_M$ increasing (semicontinuous polymerization)

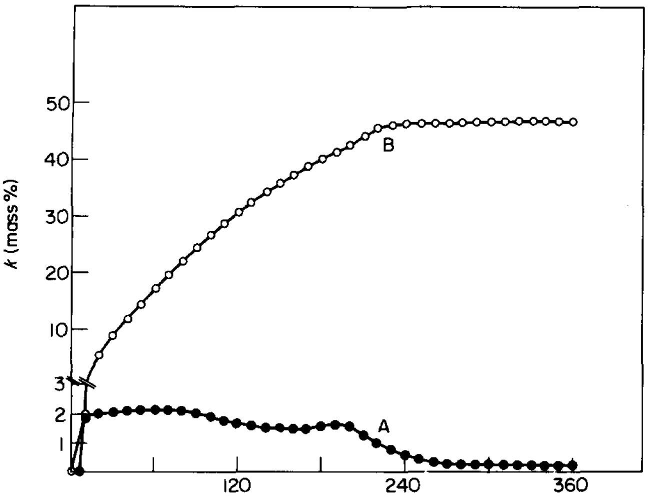

Figure 7 k_M (A) and k_p (B) *versus* polymerization time (points (●, ○) experimentally determined; (——) calculated from the velocity)

When the concentration coefficients of the different components are known, k_P or k_M or both can be determined from equation (5). Calculated and gravimetrically determined values of the monomer and polymer concentration are shown in *Figure 7*, where there is good agreement between the values. The differences between calculated and experimentally determined values of the concentration are smaller than 1%.

The most simple application of this method is in homogeneous polymerization systems. However, investigations during a VC-suspension polymerization (see *Figure 8*) indicate high sensitivity and allow the same conclusions to be drawn.

CONCLUSIONS

Ultrasonic investigations during polymerization provide information on the particle growth in the low conversion region and on the conversion in the high conversion region. Based on an empirical formula the ultrasonic velocity can be used for an analysis of the polymerization process.

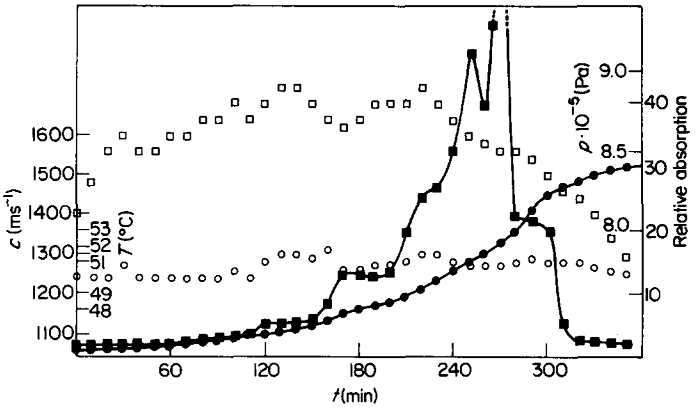

Figure 8 VC polymerization velocity with time (α values (■), velocity (●), temperature (○) and pressure (□))

The limits for the application of this ultrasonic method are following:

(1) The excess Δc, defined as the difference between the velocity values of the monomer and the polymer, must be sufficient to guarantee a high sensitivity ($\Delta c > 10\ \mathrm{ms}^{-1}$).

(2) The ultrasonic attenuation must be considerably lower, as in gaseous systems.

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