Measurement Method and Apparatus for Monitoring the Kinetics of Polymerization and Crosslinking Reactions by Microwave Dielectrometry

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Synopsis

The experimental apparatus employed for monitoring fast polymerizing and crosslinking processes is described in detail. The measurement method for the particular application is widely discussed and the resulting performances of the measurement technique are reported. As an example, the experimental results for polymerization and crosslinking reactions of n-butyl acrylate and 1,6-hexandiol-diacrylate are shown and the accuracy of the data acquisition is demonstrated.

INTRODUCTION

Dielectric analysis has been proved to be a powerful tool for investigating molecular structure and motions[1-3]; complete information on dielectric behavior of a system can be obtained from measurements performed in a wide range of frequencies, extending from DC to microwaves.[4] In addition, dielectrometry is a nondestructive method[5] and particularly convenient for measurements *in situ*.[6,7] Finally, dielectrometric analysis in itself is a characterization, from the technological point of view, of a large variety of materials and processes. In such a context dielectric monitoring of curing processes[8-10] and polymerization reactions[11-13] has gained in recent years a large deal of interest.

In a polymerizing mixture, the resulting complex permittivity is connected with two main microscopic mechanisms: dipole motion and ionic conduction, whose contributions strongly depend on the frequency of the applied electric field.[3,14] At low frequencies, the main contribution to the imaginary part of permittivity (loss factor ϵ'') comes from ionic conduction. This last depends on mobility of the ions always present in the reacting mixture as impurities, giving a significant contribution even in few parts per million.[15] Ionic mobility in curing and/or polymerizing systems is strongly affected by bulk viscosity, which increases during this kind of reactions; therefore, loss factor measurements at low frequency have been largely used for monitoring curing and polymerization processes.[14,16] The contribution of dipolar motions to loss factor can be neglected only at very low frequencies; however, in these conditions spurious contribution due to the electrode polarization becomes important.[14] On the other hand, in

the low frequency range, the contribution to real part of the dielectric constant (ϵ') of polymerizing systems comes from many dielectric polarization phenomena of both monomer and polymer molecules.[3] Therefore in such a range of frequency it is very hard to relate the ϵ' change to a specific dielectric contribution, especially during the reaction process.

At higher frequency, dielectric data for both ϵ' and ϵ'' become dominated by dipole response related to segmental and side chain motions in the macromolecule[1-3] as well as to monomer motion, the latter contribution occurring at the upper end of the frequency range (microwaves).[17] In the most cases, the dielectric contribution of the monomer dipoles is quite well separated from those of macromolecules and it can be used for monitoring the monomer concentration in the system under reaction. Microwave frequencies in the gigahertz range are particularly convenient for studying chain radical polymerizing systems such as acrylates and methacrylates,[11-13] as well as epoxy resin curing processes.[18]

Starting from these considerations, a new method for monitoring fast chain radical polymerization processes based on complex permittivity measurements of the polymerizing system at a fixed microwave frequency has been recently introduced.[11,12,19] An accurate experimental analysis on different chemical systems has been performed in order to prove the actual relationship between instant residual monomer concentration and both imaginary and real parts of the dielectric constant.[10-12] Experimental results indicate that the high frequency dielectric behavior of a polymerizing mixture allows one to employ the microwave dielectric measurements in order to follow both polymerization and crosslinking reactions.[20] Moreover, fundamental kinetic parameters, such as instant polymerization rate, induction period, and residual monomer concentration at the end of the process, can be determined by microwave dielectric method.[13] In addition, this method, with respect to others[21,22] such as infrared spectroscopy, differential scanning calorimetry, and pulsed nuclear magnetic resonance, appears very fast, accurate, and reliable. Finally, several microwave techniques appear promising for dielectric measurements *in situ* and for nondestructive monitoring of curing processes. In this paper an apparatus operating at microwave frequencies for laboratory experiments, concerning UV photoinitiated chain radical polymerization reactions, is described and discussed in detail.

EXPERIMENTAL

Measurement Method

Kinetics of polymerization reactions can be monitored by following the time evolution of the instantaneous monomer residual concentration. As mentioned above, this can be accomplished by measuring the dielectric constant of the polymerizing mixture at a proper microwave frequency. For this purpose the well-known cavity perturbation method[23] (CPM) can be applied extending it to time-dependent processes.

According to the CPM, the real (ϵ') and imaginary (ϵ'') parts of the dielectric constant ($\epsilon = \epsilon' - i\epsilon''$) of a small sample, placed right inside a cavity, can be related to the resonant frequency (ν) and Q factor[23] of the cavity (Q) by the following equations:

$$\epsilon' - 1 = -2(\nu - \nu_0)/\eta\nu_0$$
$$\epsilon'' = (1/Q - 1/Q_0)/\eta \qquad (1)$$

where ν_0 and Q_0 are the resonance frequency and Q factor of the cavity without sample, respectively, and η is the filling factor[19] of the sample, which is related to the ratio between sample and cavity volumes. Equations (1) are written for the case of static determination.

Measurements of resonance frequency can be very accurate and easily performed, whereas some difficulties can arise from determinations of Q factor (defined by the ratio between the energy stored in each wave period and the average power loss) because usually a high accuracy can be reached using a rather complex procedure only, either at fixed[24] or swept[25] frequency conditions.

However, a simpler procedure can be used when the ϵ'' determination is performed by measuring the voltage standing wave ratio[26] (VSWR) at the cavity input in resonance conditions. In fact, according to the VSWR method,[27] the second of eqs. (1) becomes

$$\epsilon'' = (\text{VSWR} - 1)/\eta Q_0 \qquad (2)$$

where $\text{VSWR} = (1 + \sqrt{P_r/P_i})/(1 - \sqrt{P_r/P_i})$, P_r and P_i being the reflected and incident powers in resonance conditions, respectively. This VSWR method allows to determine ϵ'' directly by measuring the reflection coefficient P_r/P_i of the cavity at its resonance frequency.

The first of eqs. (1) and eq. (2) can be extended to determine the instantaneous values of $\epsilon'(t)$ and $\epsilon''(t)$ in time-dependent processes, according to the following equations[19]:

$$\epsilon'(t) - \epsilon_1' = -2[\nu(t) - \nu_1]/\eta\nu_1$$
$$\epsilon''(t) - \epsilon_1'' = [\text{VSWR}(t) - \text{VSWR}_1]/\eta Q_0 \qquad (3)$$

where ϵ_1', ϵ_1'', ν_1, VSWR_1, and η are, respectively, the real and imaginary parts of the dielectric constant of the sample, the cavity resonance frequency, the voltage standing wave ratio at the cavity input, and the filling factor of the sample at the beginning of the process; $\nu(t)$ and $\text{VSWR}(t)$ are the corresponding time-dependent quantities.

The unloaded Q factor[28] Q_0 of the cavity, as well as the filling factor η, has to be measured only when absolute determinations of ϵ' and ϵ'' are requested.

For a chain radical polymerization reaction in bulk supposed to reach an ideal completion, the composition of the polymerizing system changes during the reaction time from pure monomer to pure polymer; as a consequence, the complex dielectric constant of the system changes from the starting pure monomer value ϵ_M to the final value ϵ_P of the pure polymer. Therefore, provided that the filling factor η is constant during the process, eqs. (3) can be rearranged in normalized form as follows:

$$\frac{\epsilon'(t) - \epsilon'_M}{\epsilon'_P - \epsilon'_M} = \frac{\nu(t) - \nu_M}{\nu_P - \nu_M}$$

$$\frac{\epsilon''(t) - \epsilon''_M}{\epsilon''_P - \epsilon''_M} = \frac{VSWR(t) - VSWR_M}{VSWR_P - VSWR_M} \tag{4}$$

When the process under investigation occurs with appreciable volume variation, the filling factor also changes and eqs. (4) have to be rewritten[19] as follows:

$$\frac{\chi'(t)/\rho(t) - \chi'_M/\rho_M}{\chi'_P/\rho_P - \chi'_M/\rho_M} = \frac{\nu(t) - \nu_M}{\nu_P - \nu_M}$$

$$\frac{\chi''(t)/\rho(t) - \chi''_M/\rho_M}{\chi''_P/\rho_P - \chi''_M/\rho_M} = \frac{VSWR(t) - VSWR_M}{VSWR_P - VSWR_M} \tag{5}$$

where ρ and $\chi = \chi' - i\chi''$ are the density and complex electric susceptibility, respectively. χ is related to the complex dielectric constant by means of the well-known equation $\chi = (\epsilon - 1)/4\pi$.

Taking into account that monomer and polymer have very different molecular sizes, dipolar motions of the monomer are weakly affected by viscosity in a monomer/polymer mixture.[29] In addition, if the mixture at microwave frequencies is supposed to behave like an ideal solution of a weakly polar solute (monomer) in a nonpolar solvent (polymer),[30] both the left hand sides of eqs. (5) can be related to the instantaneous number of monomeric dipoles $M(t)$,[11,19] according to the following equations:

$$\frac{\chi'(t)/\rho(t) - \chi'_M/\rho_M}{\chi'_P/\rho_P - \chi'_M/\rho_M} = \frac{\chi'(t) \cdot V(t) - \chi'_M \cdot V_M}{\chi'_P \cdot V_P - \chi'_M \cdot V_M} = \frac{M_1 - M(t)}{M_1}$$

$$\frac{\chi''(t)/\rho(t) - \chi''_M/\rho_M}{\chi''_P/\rho_P - \chi''_M/\rho_M} = \frac{\chi''(t) \cdot V(t) - \chi''_M \cdot V_M}{\chi''_P \cdot V_P - \chi''_M \cdot V_M} = \frac{M_1 - M(t)}{M_1} \tag{6}$$

where M_1 is the initial number of dipoles and $V(t)$, V_M, and V_P are the instantaneous, initial, and final volumes of the sample in that order. This does not mean that the polymerizing monomer/polymer mixture has to be ideal (absence of dielectric interactions). It is enough to detect a proper frequency at which the dielectric constant of the mixture is linearly dependent on composition.

As the monomer to polymer conversion $C(t)$ is defined as $[1 - M(t)/M_1]$ eqs. (5) and (6) can be combined as follows:

$$C(t) = \frac{\nu(t) - \nu_M}{\nu_P - \nu_M}$$

$$C(t) = \frac{VSWR(t) - VSWR_M}{VSWR_P - VSWR_M} \tag{7}$$

From a theoretical point of view both of eqs. (7) provide the same results,

the choice of one of them depending on dielectric characteristics of the system [13] under investigation, as well as on experimental conditions. As far as the latter are concerned, the acquisition time for a single measurement, temperature effect on the measured quantities, and the requirement to measure the residual monomer concentration at the end of the process are the most important.

In the practice a polymerization reaction does not attain completion, as a consequence the values of ν and VSWR at the end of the reaction are not coincident with the pure polymer values ν_P and $VSWR_P$ in eq. (7). Strictly, in order to determine the residual monomer concentration at the end of the reaction, the pure polymer values ν_P and $VSWR_P$ can be calculated from eqs. (8), obtained by manipulating the first of eqs. (1) and eq. (2):

$$\nu_P = \nu_0 + (\nu_M - \nu_0) \frac{\rho_M(\epsilon'_P - 1)}{\rho_P(\epsilon'_M - 1)}$$

$$VSWR_P = 1 + (VSWR_M - 1) \frac{\rho_M \epsilon''_P}{\rho_P \epsilon''_M} \tag{8}$$

where $\epsilon_P = \epsilon'_P - i\epsilon''_P$ and $\epsilon_M = \epsilon'_M - i\epsilon''_M$ are the dielectric constants of the pure polymer and monomer, respectively. In eqs. (8) it has been taken into account for the different densities of monomer and polymer.

When the pure polymer shows a loss factor much lower than that of the pure monomer ($\epsilon''_P/\epsilon''_M \ll 1$), as usually occurs if a proper microwave frequency is chosen, the $VSWR_P$ results close to 1 according to the second of eq. (8), and the second of eqs. (7) becomes simply

$$C(t) = \frac{VSWR(t) - VSWR_M}{1 - VSWR_M} \tag{9}$$

Equation (9) allows an accurate determination of the residual monomer concentration at the end of the process and this quantity can be used in the first of eqs. (7) in order to calculate ν_P, without using the first of eqs. (8).

When polymerization reactions are performed in the presence of a nonpolar solvent, the loss factor of the polymer cannot be further neglected and eq. (9) is no longer true. In such conditions eqs. (7) and (8) can be employed, provided that the dielectric constant and density values are referred to solutions.

The hypothesis that the monomer/polymer mixture, whose composition changes during a polymerization process in bulk, behaves like an ideal solution of a weakly polar solute in a nonpolar solvent at least at certain frequencies has to be experimentally checked. This can be accomplished, for example, by measuring the quantities on the right-hand sides of eqs. (7) for a set of monomer/polymer mixtures having known relative concentrations. This procedure has been performed in the case of n-butyl acrylate (BA)/poly(BA) mixtures at 10^{10} Hz and the detailed discussion of the results is reported in Ref. 12. Other approaches for verifying the linear dependence of dielectric measurements on conversion can be successfully adopted by comparing dielectrometry with either IR spectroscopy [11] or calorimetry [18] data.
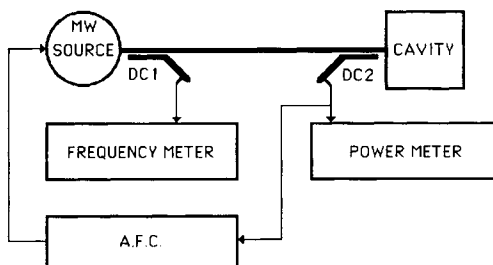
Fig. 1. Diagram of the apparatus here discussed and adopting the passive resonant principle. AFC is the device for controlling the frequency; DC1 and DC2 are directional couplers.

Measurement System

The operating principle of the experimental apparatus is shown in Figure 1. The microwave source is frequency locked, by means of an automatic frequency control loop,[31] to the reflection cavity resonating at about 9.5×10^9 Hz and containing the sample. During the polymerization, the frequency of the source exactly follows the resonance frequency shift of the cavity and both instantaneous power reflected from the cavity and frequency are measured. The corresponding instantaneous dielectric quantities, $\epsilon'(t)$ and $\epsilon''(t)$, are calculated according to eqs. (3). Such operating principle is named "passive resonant" because the frequency locking is achieved by an electronic system, the microwave circuit playing a passive role.

A different operating principle could also be used, as shown in Figure 2, where a transmitting cavity inserted in the feedback loop of a microwave amplifier allows the self-oscillation of the system at the resonance frequency of the cavity (active resonant apparatus).[32,33] Also in this case, for determining the dielectric constant according to eqs. (3), both frequency shift and power reflected from the cavity have to be measured.

For dielectric measurements in time-dependent processes, both active and passive resonant methods can be usefully employed. The active resonant method shows two important advantages: the use of few microwave components and the achievement of frequency-locking with a very fast capture time. However, for measuring with high accuracy the true resonant frequency and power
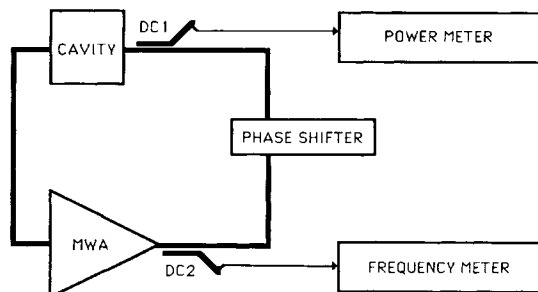
Fig. 2. Diagram of an apparatus adopting the active resonant principle. MWA is a microwave amplifier; DC1 and DC2 are directional couplers.

reflected from the cavity, the loop phase shift has to be minimized, as the frequency changes, by means of an electronically tunable phase shifter.[32,33] In this case the advantages previously quoted are lost and the passive resonant method results more suitable.[27]

In conclusion an apparatus for laboratory measurements takes advantage by using the passive resonant method, although very interesting and simple apparatus could be built up by using the active resonant method, especially for monitoring industrial processes and for *in situ* measurements.

The block diagram of the complete apparatus employed in experiments reported here is drawn in Figure 3. The apparatus, based upon the passive resonant method, is specialized for studying the kinetics of fast radical photoinitiated polymerization reactions and for measuring the microwave dielectric constant of liquids, in particular of monomer/polymer mixtures.

The employed microwave source is the sweeper EIP 925, set to emit a microwave power of about 1 mW. Different sources can be also usefully employed, such as several solid state oscillators and klystrons. The frequency locking is achieved by modulating the frequency of the source at 10^4 Hz and by detecting the amplitude modulated microwaves that are reflected by the cavity at resonance. This detection is performed by means of a zero-bias diode MA 7744A, thus avoiding any polarization. The detected signal at 10^4 Hz is passed through an RC passive passband filter and amplified by the differential amplifier Tektronix Model 7A22; after that the signal is phase-detected by means of the lock-in amplifier PAR Model 5206. The total amplification of the loop is about 150 dB.

The incident and reflected powers from the cavity are decoupled from each other by means of the circulator MA Model 8M212, which performs the same

Fig. 3.   The block diagram of the apparatus: (DC) directional coupler; (C) circulator; (LM) light monitor; (D) zero-bias diode; (H) head of the power meter; (A) matched termination.

decoupling on the third port too. Finally the residual reflected power is dissipated in the matched termination on the fourth port. The power reflected from the cavity is passed through a 6 dB directional coupler and thus decoupled from the spurious power reflected from the detector assembly. Then a 10 dB attenuator properly limits the measured power in order to use the full dynamic range of the power meter Marconi Model 6960 with the head Model 6920.

By this experimental setup the power reflection coefficient at the cavity input is simply measured. A fraction of the reflected power from the resonant cavity is continuously measured during the process, whereas the same fraction of the incident power is measured at the end of the process simply by short-circuiting the cavity input. In fact, the long-term stability of the power emitted from the microwave source employed is better than the accuracy of power measurements themselves, thus making meaningless the procedure of simultaneous measuring of the incident and reflected powers.

The resonance frequency is measured at the reference output of the microwave source by the frequency meter Systron Donner Model 6054B.

The liquid samples, which have to be submitted to a polymerization process initiated by UV-light irradiation, are contained in a quartz cuvette placed in the center of the cavity (Fig. 4). Such a cuvette has a right cylindrical shape with the volume of 10 μL; the thickness of the sample contained is 0.3 mm in order to keep the light path length small enough to satisfy the condition of low light absorption.[12]

The assemblage of the cavity is drawn in Figure 4. The requested thermal stability is achieved by coiling around the cavity a pipe of silicone rubber in which thermostated water flows. Inside the cavity some boundary conditions for the microwave electric field have to be verified and all the shapes of the items placed inside the cavity must be matched with the electric field distributions in order that eqs. (1) may hold. In the right cylindrical TE_{011} cavity we have employed, all shapes must have cylindrical symmetry with the axis lying on the axis of symmetry of the cavity. The influence of boundary conditions on the overall accuracy of measurements is discussed elsewhere.[19,23,34]

The UV light is obtained by a high pressure mercury lamp Osram HBO 100W mounted in lamp housing supporting an elliptical mirror, filter holders, an electromechanical shutter, and a light intensity measuring system. The light
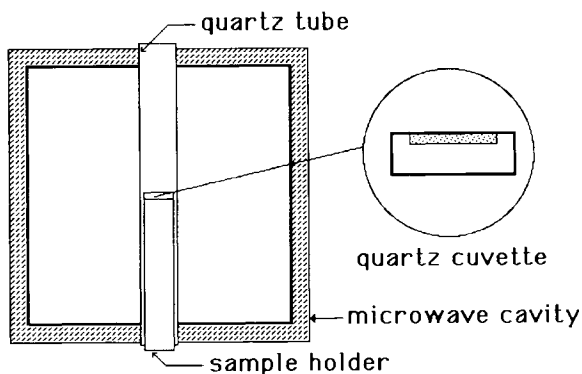

Fig. 4. The assemblage of the cavity.

emitted from the lamp is at first filtered by passing it through a circulating water filter, in order to lower infrared contents; then a glass colored pass-band filter, Melles-Griot Model 03FCG179, at 330 nm with a width of 90 nm, is provided to enhance the intensity of spectral content in the range of interest. The intensity of the UV emission can be varied by using a set of light precision UV neutral density filters Melles-Griot Model 03FNQ and/or by defocusing the elliptical mirror which collects the light emitted from the lamp. The irradiation of the sample is obtained via the quartz light guide which can easily be introduced in the cavity. Before starting the experiment the light intensity is measured in the position of the sample by an UV silicon photodiode Centronic Model OSD1-1R2, NBS calibrated, whereas during the experiment a fraction of the light is monitored by means of a beam splitter and a photodiode mounted on the lamp housing. The photodiodes are used in photoconductive mode and resulting voltages are measured by the voltmeter Solartron Model 6070. The home-made electromechanical shutter is controlled by the computer and its switching times are shorter than 10^{-2} s.

Usually the photoinitiated polymerization experiments have been performed at 25°C; the temperature is controlled by means of water flow from a thermostatic bath having a long term stability of ±0.02°C. The temperature is measured by means of a meter for thermocouples Fluke Model 2190A with the resolution of ±0.1°C.

During the polymerization process, a thermostatted slow flow of an inert gas (N_2 or He) is provided in order to remove the heat in excess produced by the exothermic reaction and to avoid any contact of the sample with the oxygen, which inhibits the reaction. The cooling system here adopted, due to the small volume of sample with respect to its very large surface, efficiently removes the heat so that the sample temperature is kept constant at (25 ± 0.1)°C.

Interactive software has been developed for the computer IBM PC in order to manage the data acquisition and data processing.

RESULTS AND DISCUSSION

The dielectric method for monitoring the kinetics of polymerization reactions has been discussed in previous papers[11,12,13]; here we will discuss the performance of the experimental apparatus and some details about the measurement procedure. In our experiments the monomer to polymer conversion is determined by means of resonance frequency and power reflection coefficient measurements according to eqs. (7). Such measurements are influenced by several spurious effects which have to be taken into account in order to obtain the requested accuracy. The temperature fluctuations of the cavity affect directly the resonance frequency; the Q factor of the cavity, the noise of the microwave source, and electronic apparatus employed affect the stability of the frequency locking loop. The variation of the resonance frequency of the cavity when temperature changes can be calculated at first approximation by measuring the temperature coefficient for the resonance frequency. For the aluminum made cavity we employ (Q factor of 12000), a temperature coefficient of 2×10^5 Hz/°C has been measured.

The FM modulation of the microwave source is chosen to be 10^4 Hz in order to keep sideband inside the spectral bandwidth of the emitted central frequency

and then to maintain spurious reflected power, at resonance condition, below the requested level. The gain and frequency response (of phase locking loop must be chosen as highest as possible providing that the stability criteria discussed in Ref. 35 are fulfilled.)

By taking into account the above requirements, the best performance of the apparatus is achieved. This performance can be determined by measuring the overall frequency stability affected by both long- (temperature drift) and short-term (noise of the frequency locking loop) effects. The frequency stability has been evaluated by measuring the resonance frequency in the band 1.7×10^{-3}–1 Hz, where only long-term effects are effective (Fig. 5). Experimental data show small deviations around a substantial linear trend, thus suggesting the evaluation of the stability in terms of standard deviation in the linear fit of the data. In fact, the observed frequency shift is lower than 4 kHz and corresponds to a temperature drift of the cavity of about 0.02°C, according to the measured temperature coefficient, and the calculated standard deviation is 50 Hz. In our experiments, frequency shifts of that order do not affect the requested accuracy; otherwise a monitoring of the cavity temperature can be easily accomplished in order to compensate the measured frequency for the long term shifts.

For frequency measurements the acquisition time depends on the chosen frequency resolution. In a typical polymerization experiment the frequency changes of about 2×10^6 Hz; then a resolution of about 10^3 Hz was enough for practical purposes. Of course, more accurate experiments can be performed by choosing higher resolution, that is, 10^2, 10, or 1 Hz, by taking into account for long-term accuracy of frequency measurements, as discussed above. This value corresponds, according to the first of eqs. (7) and for a reaction in bulk, to a sensitivity on the conversion C better than 10^{-4}. Such a sensitivity is reduced by the relative volume fraction of the solute when the reaction occurs in solution.

For power measurements the acquisition time cannot be shorter than 2.5 $\times 10^{-2}$ s and the minimum power resolution is 0.1×10^{-9} W. In our experiments the sensitivity on the conversion C ranges between 10^{-3} and 10^{-5}, depending on the power reflection coefficient values, according to the second of eqs. (7). It has to be pointed out that the power reflection coefficient of the cavity is
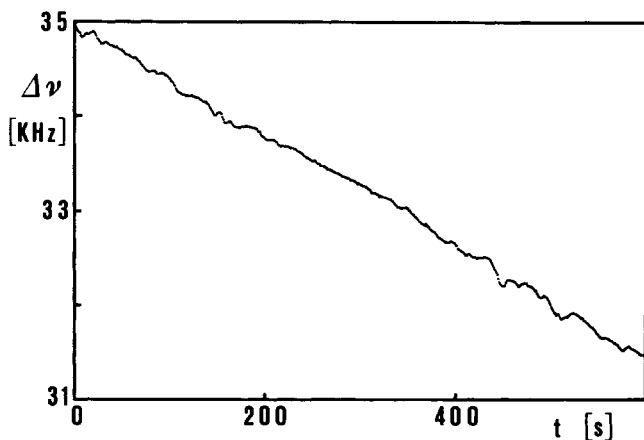

Fig. 5.   Measurement of the long term frequency stability.

almost independent from temperature variations, which on the contrary greatly affect the resonance frequency due to thermal expansion of the cavity. The data are collected and transferred via standard digital interfaces IEEE-488; the data transfer time requested for a single measurement is about 10^{-2} s.

The apparatus here discussed has been widely employed for monitoring different photoinitiated polymerization reactions both at low[10,12,35] and high[13] conversions. In Figure 6 the residual monomer concentration $(1 - C)$ for two different polymerizing systems is plotted as a function of UV irradiation time t; in this case the quantity C has been calculated by using eq. (9) and the acquisition rate is 10 samples/s. The experimental data for the polymerization reaction of n-butyl acrylate (BA) in 2-methylundecane solution in the presence of 2,2-dimethoxy-2-phenylacetophenone (DMPA) as photoinitiator are drawn in curve 1; curve 2 refers to the polymerization reaction in bulk of BA/1,6-hexandiol-diacrylate (HDDA) equimolar mixture in the presence of 1-hydroxycyclohexyl phenyl ketone as photoinitiator. The sample of HDDA/BA has been prepared in air in order to show that the technique can measure the induction period of reaction, due to the oxygen dissolved in the sample. In both experiments the final residual monomer concentration is well determined.

The experimental data reported in Figure 6 can be further treated for calculating the behavior of the polymerization rate dC/dt during the whole process (Fig. 7); moreover, this result, being obtained from a first derivative of experimental data, shows the overall accuracy of the measurements.

In Figure 8 a different plot of the experimental data is drawn in order to show the two different reaction mechanisms involved. In fact, the plotted quantity $(dC/dt/(1 - C)$ depends directly on propagation and termination constants of reaction.[13] Therefore, in the case of polymerization of a monofunctional monomer, such as of BA in solution, the above quantity is almost constant up to high conversion values: On the contrary, in the case of photocrosslinking reaction of HDDA/BA, autoacceleration phenomena occur and the plotted
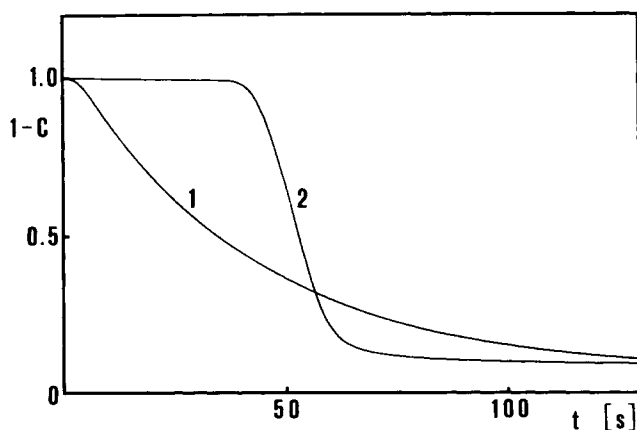

Fig. 6.   Dielectric measurements of $(1 - C)$ vs. time: (1) photoinitiated polymerization of BA in 2-methylundecane solution ([BA] = 3.5 mol/L) in the presence of 1.4×10^{-2} mol/L of DMPA under 44 W/m^2 UV light irradiation intensity; (2) photoinitiated polymerization of HDDA/BA mixture (1 : 1 molar) in the presence of 2.5×10^{-2} mol/L of 1-hydroxycyclohexyl phenyl ketone under 12 W/m^2 UV light irradiation intensity.
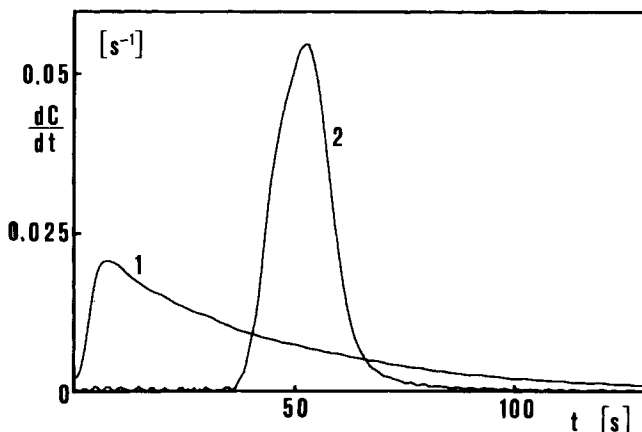
Fig. 7. dC/dt vs. time, calculated from the data of Figure 6.

quantity increases up to a maximum value of about $C = 0.7$; after that it rapidly goes down.

CONCLUSIONS

The microwave apparatus here described has been proved to be very suitable for measuring the residual monomer concentration, provided that the system submitted to the reaction has been characterized from a dielectric point of view; in any other case it can be usefully employed to monitor with high sensitivity the process under consideration.

The measurement method has been developed especially in order to perform fast and accurate measurements of both the real and imaginary parts of the microwave dielectric constant of systems submitted to physicochemical pro-
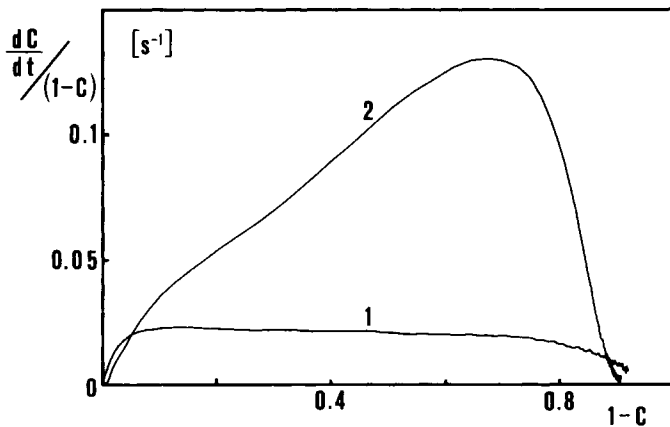

Fig. 8. $(dC/dt)/(1 - C)$ vs. C, calculated from the data of Figure 6.

cesses, such as photoinitiated polymerization and photocrosslinking of acrylic monomers.

Here an apparatus for laboratory applications is presented in detail and some suggestions are given in order to build up apparatus for monitoring industrial processes. In particular, the microwave dielectrometry appears to be a very promising and a powerful tool for monitoring *in situ* industrial processes by using either cavity or free space methods.

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