Variation of the microwave dielectric permeability of the acrylamide—calcium nitrate system during its spontaneous polymerization

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The kinetics of the variation of the complex dielectric permeability at microwave frequencies of 1.1, 1.7, 2.7, and 10 GHz during spontaneous polymerization of acrylamide in the presence of the hydrate of calcium nitrate was studied. The microwave conduction of this system has an ionic nature. It was assumed that some of the water liberated during the polymerization is both transformed into a bound state and forms microinclusions of an electrolyte solution in the bulk of the polymer.

Key words: acrylamide, calcium nitrate, polymerization, complex dielectric permeability, conduction, microwave.

In recent years, considerable interest has been generated in the polymerization of complexes of crystal hydrates of metal nitrates with acrylamide due to the discovered thermally induced frontal and spontaneous polymerization at room temperature.[1,2] Water of crystallization participates in the polymerization and plays an important role in it.[3] It is also known that the dielectric permeability of water undergoes a dispersion in the microwave region, and therefore its molecules can serve as a kind of "probe" for structural rearrangements occurring during polymerization, which permits the use of dielectric microwave spectroscopy for the investigation of this process. Moreover, the dielectric properties of metal-containing polymers in the microwave range, which are of interest in themselves, have not been studied.[4,5] An exception is the tentative result[2] obtained in the measurement of the kinetics of the dielectric permeability of acrylamide—chromium nitrate and acrylamide—bismuth nitrate systems during their spontaneous polymerization at a frequency of 2.7 GHz. It was noted that the imaginary part of the dielectric permeability ε'' increased dramatically (by ~20 times) after the complex formation, but no explanation of this fact was presented.

In the present paper, we discuss the results of an experimental study of the variation of the complex dielectric permeability (DP) in the microwave range during the spontaneous polymerization of acrylamide (AAm) in the presence of $Ca(NO_3)_2 \cdot 4H_2O$.

Experimental

The $Ca(NO_3)_2 \cdot 4H_2O$—AAm system for the polymerization was prepared from reagents of the "pure for analysis" and "pure" grades in 1 : 3 and 1 : 8 molar ratios (systems I and II, respectively).[2] After separation of the water of crystallization, the samples were placed in glass tubes with diameters from 0.2 to 1.2 mm, depending on the frequency range and on the magnitude of dielectric losses in the samples. The real ε' and imaginary ε'' parts of the complex dielectric permeability were determined on an automated radiophysical test bench by a modified resonance procedure[2] at frequencies of ~1.1, 1.7, 2.7, and 10 GHz. The time required for passing the resonance curve is ~1 s. The accuracy of the measurement of ε' is 5 %, that for ε'' is 10 %. Each point in the experimental curve is the average value over 3—10 measurements carried out at intervals of 20—30 s. The experiments were carried out at 21—23 °C and a relative moisture of 45—55 %. The maximum warming-up of the sample (measured by a thermocouple) during polymerization did not exceed 1 °C. To inhibit the polymerization up to the beginning of the measurements (~10 min), ~0.01 % phenothiazine was added to the mixture as an inhibitor. Evaporation of water was monitored gravimetrically and did not exceed 0.1 %.

Results and Discussion

Figure 1 presents typical kinetic curves for the variation of ε' and ε'' during the spontaneous polymerization of the $Ca(NO_3)_2 \cdot 4H_2O$—AAm system at frequencies of 1.1 and 10 GHz. Note the characteristic difference in the behavior of ε' and ε'' in the low-frequency (LF) and high-frequency (HF) regions of the microwave range. For example, whereas substantial variations of the DP can be seen at 1.1 GHz (ε' changes ~1.4-fold and ε'' changes ~6-fold), at 10 GHz these variations are slight. Note also that the ε'' value at a frequency of 1.1 GHz in the initial stage of the spontaneous polymerization is almost 2.5 times higher than the dielectric losses in pure water ($\varepsilon'' = 5.5$)[6] (the initial dielectric permeabilities of the components of the mixture were as follows: for calcium nitrate $\varepsilon' = 6.2$ and $\varepsilon'' = 0.2$, for AAm, $\varepsilon' = 2.4$ and $\varepsilon'' = 0.16$). Another characteristic feature of the

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 872—875, April, 1996.

1066-5285/96/4504-0827 $15.00

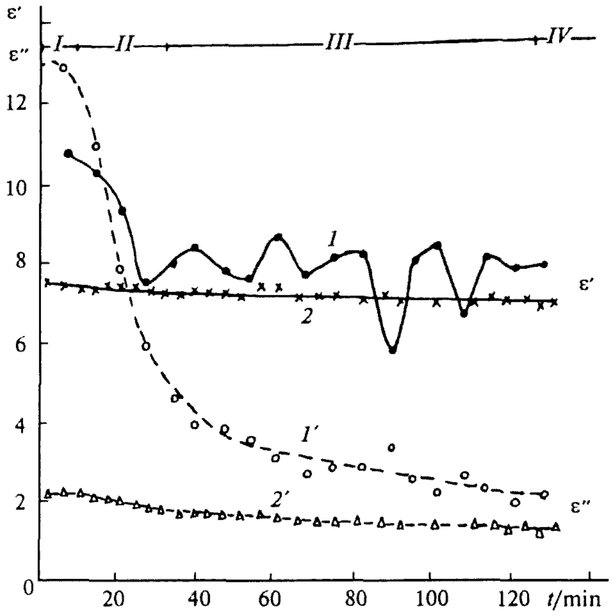

Fig. 1. Time dependence of ε'(*1*, *2*) and ε''(*1'*, *2'*) during the spontaneous polymerization of mixture I at frequencies ~1.1 (*1*, *1'*) and ~10 (*2*, *2'*) GHz.

curves obtained is the presence of out-of-the-line points of ε' differing in amplitude and position from sample to sample. In some cases, the difference in the ε' values between neighboring points is ~5 times greater than the error of the measurements; the deviations of the outlying ε'' values are close to the error of the measurements. They decrease with an increase in the electromagnetic field frequency (see Fig. 1, curves *1* and *2*). In systems that do not polymerize, no outliers are observed.

In all cases of monitoring the DP, the maximum rate of variation of ε'' was achieved after 15—20 min (by this time, the temperature of the sample was virtually maximum, $\Delta T \approx 1$ °C), but 120—140 min later the variations were slight. At this time hardening of the sample was largely completed. The ε'(*t*) and ε''(*t*) values at frequencies of 1.7 and 2.7 GHz occupy an intermediate position between those shown in Fig. 1; the absolute values of ε' and ε'' in the system II are ~20—30 % lower than those in the system I.

A number of regions can be conventionally distinguished in the frequency dependences of the ε'(*t*) and ε''(*t*) kinetic curves, which reflect complex relaxation curves in the polymerizing system. These regions are seen most clearly in the ε''(*t*) curves (see Fig. 1): *I* is the region corresponding to the induction period caused by the effect of the inhibitor added, *II* is the region of rapid changes in ε''(*t*), *III* is the region where the curve flattens out, and *IV* is the region of slow changes. To construct the frequency dependences of ε'(*f*) and ε''(*f*), we formally chose characteristic periods within these regions: t_1 is the time of the beginning of measurements, which is ~3—8 min after mixing the components of the system; t_2 corresponds to the maximum rate of variation of ε''(*t*) (~15—20 min); t_3 is the time of flattening-out (estimated from the intersection of the tangent drawn at the point of the maximum change of ε''(*t*) with a tangent to region *IV*) (~30—60 min); and t_4 is the conventional time of the beginning of region *IV* (~120—140 min). The decrease in ε''(*t*) in this region is no more than 5 % over a period of ~14 h, which makes it possible to evaluate t_3. Fig. 2 presents the frequency dependences of DP for times t_1 and t_4 characterizing the beginning and end of rapid changes in ε''.

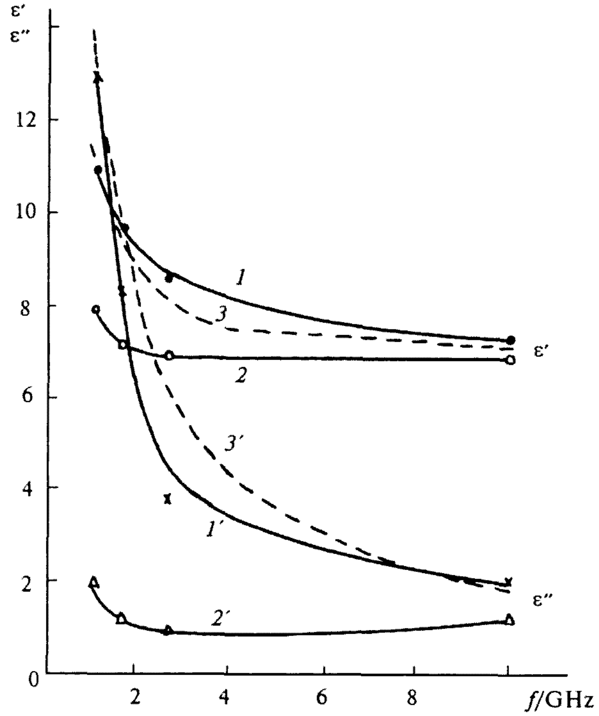

Fig. 2. Frequency dependence of ε'(*1*—*3*) and ε''(*1'*—*3'*) of mixture I for periods of time t_1 (*1*, *1'*) and t_4 (*2*, *2'*) and the dependence calculated from Eqs. (1) for time t_1 at σ = 0.43 Ohm^{-1} m^{-1} (*3*, *3'*).

A common feature of all the regions distinguished is a decrease in ε' with an increase in the frequency, which is equal to ~30—35 % for time t_1 and ~5—10 % for t_4. The dependence of ε'' on frequency is more complex. Whereas a sharp decrease in ε'' with an increase in frequency (almost sixfold over the range in which the measurements were carried out) is characteristic of time t_1, the value of ε'' virtually does not change in the HF-region during time t_3 and markedly increases during t_4.

The high values of the components of DP suggest that the greatest contribution to the DP of the system is made by the water and its state; therefore, it is natural to compare the results obtained with the Debye theory of dipole relaxation,[7] without complicating the consideration by the use of modified Debye equations for multicomponent and heterogeneous systems with a set of relaxation times[7—9] and by distinguishing the "average" relaxation time. In this case, expressions for the components of the complex DP are written in the following form:

$$\varepsilon' = \varepsilon_{00} + \frac{\varepsilon_0 - \varepsilon_{00}}{1+\omega^2\tau^2}, \quad \varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_{00})\omega\tau}{1+\omega^2\tau^2}, \qquad (1)$$

where ε_0 and ε_{00} are static and limiting high-frequency DP, respectively; $\omega = 2\pi f$, f is the frequency of the electromagnetic field; τ is the relaxation time.

The experimental $\varepsilon'(f)$ and $\varepsilon''(f)$ dependences obtained for characteristic times t_1, t_2, t_3, and t_4 were compared to those calculated from Eq. (1), using a PC, by selecting the ε_0, ε_{00}, and τ parameters.

The high value of ε'' and its frequency dependence, which differs markedly from (1), indicate that the conduction of the system may contribute to ε''. To verify this suggestion we determining the complex DP in a water-swollen polymer obtained from mixture I prior to and after the washing-out of Ca ions[10] (polymer : water ratio 1 : 9). The results are shown in Fig. 3. Whereas in the absence of Ca ions, the frequency dependences of ε' and ε'' are close to those for the DP of water[6] and can be described by formulas (1), in the presence of these ions, the frequency dependence of ε'' is close to the $1/f$ plot typical of conducting dielectrics.[7] This indicates that the conduction of the system formed has an ionic nature. Replacement of calcium nitrate by erbium(III) nitrate incorporating the metal, whose atomic weight is almost 4 times as great as that of calcium, leads to a 2.9-fold decrease in ε'', which also supports our conclusion. The introduction of an additional term $\sigma/\varepsilon_v\omega$ (ε_v is the electric constant) that takes into account the conductivity of a heterogeneous medium[7,8] to the expression (1) for ε'' leads to good agreement of the calculated frequency dependences of ε'' with the experimental curves (see Fig. 2, Table 1). The presented σ values are close to the conductivity values obtained[11] from the measurements at direct current. However, the decrease in the microwave conductivity during the spontaneous polymerization occurs approximately 4—10 times more slowly than that described previously.[11] The reasons for this deceleration will be discussed below.

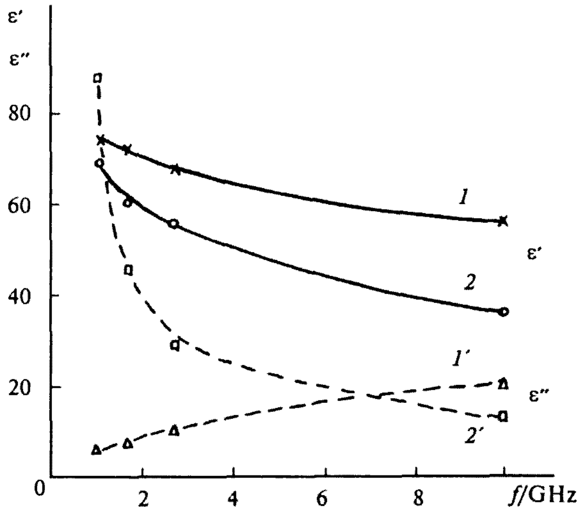

Fig. 3. Frequency dependence of ε' (*1*, *2*) and ε'' (*1'*, *2'*) for a water-swollen polymer from which calcium nitrate was washed out (*1*, *1'*) and in the presence of calcium nitrate (*2*, *2'*).

Table 1. Calculated values of the τ, σ, ε_0, and ε_{00}* parameters

Period of time	Mixture	τ /ps	σ /Ohm^{-1} m^{-1}	ε_0	ε_{00}
t_1	I	220	0.43	20	7
	II	350	0.36	20	5.5
t_2	I	150	0.35	14	6.5
	II	200	0.20	13	5
t_3	I	60	0.23	9.5	6.5
	II	90	0.07	8.5	5
t_4	I	25	0.10	8.5	6
	II	10	0.03	5.5	4.5

* The values of the parameters obtained τ = 8.5 ps, ε_0 = 80, ε_{00} = 4 for tridistilled water are close to the literature data.[6,8,13]

The frequency range in which ε'' decreases narrows down during the spontaneous polymerization. This is probably due to two processes that occur during the reaction. Initially, when the calcium nitrate hydrate was mixed with AAm, the water of crystallization was liberated, and an electrolyte solution with a high conductivity was formed, the curve for ε'' is close to $1/f$ virtually over the whole frequency range measured. As the polymerization proceeds, microinclusions (clusters[12]) of water arise, for which $\varepsilon'' \sim f^{0.8}$ in the frequency range under consideration.[13] Consequently, during the spontaneous polymerization, a frequency rise of ε'' occurs in the HF region. Calculations performed according to the model of effective dielectric medium[14] with microinclusions of water also indicate that the ε'' values increase in the HF region, if the size of microinclusions is no more than ~1 mm. This phenomenon cannot be explained by the relaxation retardation effect (increase in conductivity of an electrolyte solution with increase in frequency),[15] since the estimates show that a noticeable increase in $\varepsilon''(f)$ can be expected in this case only at frequencies above 50 GHz.

The appearance of outliers of the DP on the kinetic curves may be due to several reasons. First of all, the outliers of the ε' values and their frequency dependence may be affected by the transition of water from the free state ($\varepsilon' \approx 80$) to the bound state ($\varepsilon' \approx 3$) and back; the ε' value of water has a substantial variance in the frequency region under consideration, which leads to a decrease in the amplitude of the outliers in the HF section of the range considered. The outliers of the ε'' value should not be noticeably affected by the change in the state of water, since the ε'' value is small. At the same time, the outliers of ε'' may be caused by the instability of the conduction of the system and by the related frequency dependence of ε″. Second, the variation of ε′ and ε″ can be affected by the local appearance and disappearance of a crystalline phase[16] (a redistribution of relaxation times occurs[7]) and by the formation of gas bubbles and defects during the polymerization (which changes the effective volume of the sample). Their appearance may be due to the change in the volume during the hardening of the polymer.[17]

Table 1 presents the parameters of Eqs. (1) and the σ values that led to the best fit of the calculated and experimental data for times t_1—t_4. In general, the theoretical and experimental curves for times t_1—t_4 agree with an accuracy of ~10—35 %. This discrepancy can be explained by the fact that the calculations are approximate and do not take into account the distribution of relaxation times,[7—9] which can occur in a heterogeneous system. However, apparently, the presented parameters mainly describe quite correctly the characteristic features of the variation of the complex DP during the spontaneous polymerization.

According to Table 1, the τ, σ, and ε_0 values decrease during the spontaneous polymerization, while the ε_{00} values remain practically invariable. This behavior can be explained by the formation of microinclusions of an electrolyte solution in the sample during the polymerization. Initially (in the period of time t_1), after mixing the components and liberation of the water of crystallization, a viscous saturated solution of the salt and acrylamide with maximum τ, σ, and ε_0 is formed. The greater τ value and the smaller σ value in the case of system II is due to the higher viscosity of this mixture. During the polymerization, most of the water passes to a bound state (for example, in complexes[1,2]), and a small portion is separated as microinclusions of an electrolyte solution, whose viscosity is lower than that of the starting system (the available data do not make it possible to evaluate this portion). Consequently, the ε_0 and τ values decrease during the polymerization. The same effect can also result from an increase in the concentration of the electrolyte in the microinclusions.[8] The formation of microinclusions leads to a decrease in the ripple-through conduction and accounts for the fact that in the microwave region, the decrease in the conduction during the polymerization occurs much more slowly (~10-fold) and remains at a higher level than that measured at a direct current.

The authors are grateful to D. A. Kritskaya and V. A. Tarasenko for useful discussion of this work.

The work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 93-03-4162).

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Received February 23, 1995;
in revised form October 9, 1995