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DIELECTRIC RELAXATION OF POLYSTYRENE DOPED WITH POLAR DR1 MOLECULES

Four relaxation processes identified in polystyrene containing 2 wt % of DR1 chromophore were studied by the dielectric spectroscopy in the frequency range from 1 Hz to 1 MHz at constant temperatures from 30 to 130 °C and by thermally stimulated depolarization current measurements at sub-zero temperatures down to —160 °C. Hamon's transformation of isothermal depolarization currents were also performed to give information on dielectric relaxation at infra-low frequencies. It has been found that distribution of relaxation times related to α relaxation becomes wider due to presence of dye molecules, while both the dielectric constant and the dielectric strength increase. Considerable narrowing of the loss peak was observed with increase of temperature indicating that the PS/DR1 system is not the thermoreologically simple one and temperature-time superposition principle is not applicable above glass transition where the temperature dependence of the relaxation time obeys Williams—Landel—Ferry law. It has been found that Arrenius law is valid below glass transition.

1. INTRODUCTION

It is known that the relaxation behavior of dye molecules in guest-host polymer systems is related to molecular motion in the host polymer [1]. From another side, addition of a foreign substance to polymer modifies its relaxation behavior. These processes in nonlinear optical (NLO) polymers are interrelated and both affect stability of the poled order.

In this study we deal with a system obtained by doping pure atactic polystyrene (PS) with disperse red 1 (DR1) chromophores and called thereafter PS/DR1 system. The main transitions in amorphous PS are well established and described. The α process is observed near glass transition temperature $T_g \sim 90$—105 °C and corresponds to microbrownian motion of the main chain with apparent activation energy of 3.5 eV. The β transition is suggested to involve local motion of chain segments. It is seen at sub-T_g temperatures from —10 to +60 °C. Near T_g, α relaxation is mixed up with β process having the activation energy of 1.3—1.7 eV. The cryogenic γ and δ transitions are caused correspondingly by rotation and wagging motions of phenyl rings. The γ process is observed at about —120 °C with activation energy of 0.35—0.55 eV, and δ relaxation occurs near —230 °C with activation energy of 0.1 eV.

The data available in literature concerning relaxation processes in PS/DR1 system are limited. Nevertheless, it is recognized that glass transition phenomenon (a relaxation) plays a dominant role in affecting orientational stability of NLO dipoles. At the same time, it has been found [2] that the frequency range over which the dye relaxation occurred is similar to that typical for β transition at sub-T_g temperatures. The rotational reorientation dynamics of DR1 doped in PS have been monitored by the second harmonic generation (SHG) measurements [3] and Kohlrausch—Williams—Watts (KWW) stretched exponential has been used to fit decay of SHG signal with time at different temperatures, but the power coefficient appeared to be strongly temperature dependent. KWW expression has been also used as the response function to fit the results of dielectric measurements performed above T_g. The temperature dependence of relaxation time τ in this range has been successfully described by Williams—Landel—Ferry (WLF) equation

$$\log \frac{\tau(T)}{\tau(T_g)} = -\frac{C_1(T - T_g)}{C_2 + T - T_g} \qquad (1)$$

with $\tau(T_g) = 200$—300 s, $C_1 = 15$, $C_2 = 40$ °C, $T_g = 94$ °C. The dielectric spectroscopy of PS doped with 4′(diakylamino)-4-(methylsulfonyl) azobenzene performed at 120—140 °C gave results similar to that of PS/DR1 [3] in relation to WLF parameters. Below T_g, Arrenius function seemed to be more appropriate.

Dielectric relaxation studies are usually performed by thermally stimulated depolarization (TSD) current measurements and by AC dielectric spectroscopy in either frequency or temperature or time domain. In TSD method, the sample is poled and cooled down under applied field to freeze polarized state with the preferential orientation of dipoles. Then depolarization current is measured during linear heating in order to register peaks appearing near transition temperatures. The equivalent frequency of TSD measurements is about 10^{-3} Hz. In the case of AC di-

electric spectroscopy in frequency domain, the real (ε') and the imaginary (ε'') parts of complex dielectric constant are measured at constant temperature. In the case of Debye's process with single relaxation time, ε' and ε'' are given by

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

where $\omega = 2\pi f$; τ is relaxation time; ε_∞ and ε_s are optic and static dielectric constants correspondingly, f is frequency. The relaxation process is usually seen as a loss peak at $\varepsilon''(f)$ curve, but it appears at higher temperatures than TSD current peak. To study relaxation processes in detail, one needs to use wide range of frequencies. However, at very low frequencies, apart from technical difficulties, a serious problem arises, because relaxation component of loss peak is suppressed by the conductivity one. To avoid the difficulty, it was suggested to calculate $\varepsilon''(f)$ dependence from isothermal depolarization current curves. To cover wide ranges of temperature and frequency, we used all three abovementioned methods in the present study, namely TSD current measurements at sub-zero temperatures, the traditional AC dielectric spectroscopy and Hamon method.

2. EXPERIMENTAL

Atactic amorphous PS ($M_w = 50\,000$) was obtained by purification of commercial resin. Samples were prepared from a mixture of PS and the disperse red 1 (DR1) dissolved in chloroform and spread over glass plate. Prior to removing the film by immersing the plate into water, the samples have been treated at 100 °C for 24 h under vacuum. 20 μm-thick films contained 2 wt % of DR1. The samples of pure PS have been prepared in the similar way. It has been found using X-ray diffraction and differential scanning calorimetry that polymer films are entirely amorphous with glass transition temperature T_g around 90 °C. Aluminum electrodes of 2 cm^2 have been deposited on both surfaces of the sample by thermal evaporation in vacuum.

AC dielectric spectroscopy experiments have been performed by measuring $\varepsilon'(f)$ and $\varepsilon''(f)$ dependencies in the range from 1 Hz to 1 MHz at constant temperatures from 30 to 130 °C. To obtain TSD currents at sub-zero temperatures, the samples were poled at room temperature (300 V for 10 min) and cooled to —160 °C by immersing the sample holder in liquid nitrogen with poling field still applied. Then the films were short-circuited and reheated at constant rate of 3.5 °C min^{-1}. The isothermal depolarization currents at different constant temperatures from 20 to 125 °C necessary for Hamon transformation have been measured after short-circuiting of the samples poled isothermally for about 10^4 s at 200 V.

3. RESULTS AND DISCUSSION

3.1. Thermally stimulated currents. TSD current curves for pure and doped PS at sub-zero temperatures are shown in Fig. 1. There are four peaks on curves obtained with both materials, but position and amplitude of the peaks are different. In pure PS the peaks are seen at —5, —28, —63 and —137 °C, while in doped PS the corresponding peaks are positioned at —15, —30, —61 and —129 °C. The peak at the lowest temperature (Fig. 1) corresponds most probably to γ relaxation, while that near zero can be attributed to space charge, interfacial and/or electrode phenomena (ρ peak).

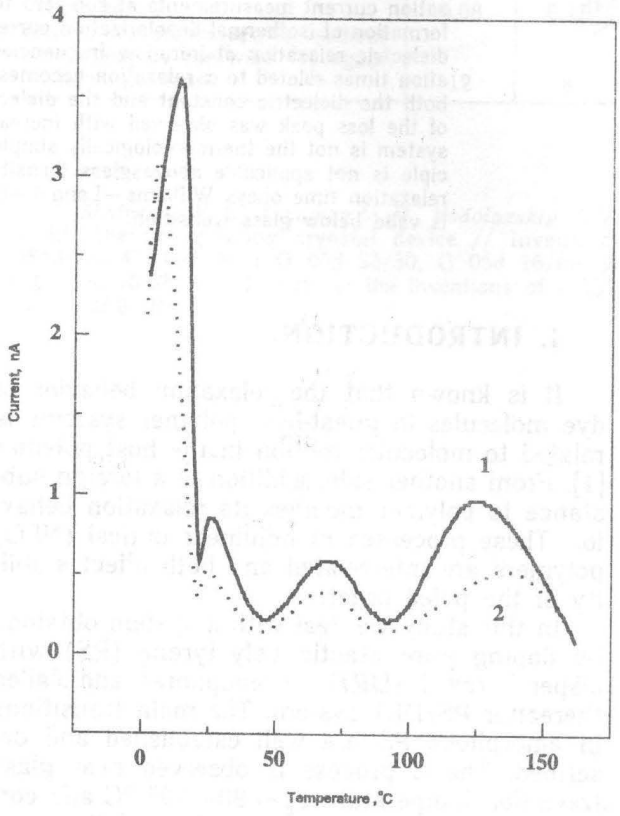

Fig. 1. Thermally stimulated depolarization currents of PS/DR1 and pure PS samples at sub-zero temperatures

The origin of the TSD current peaks around —30 and —60 °C is not clear, but they are probably related to β processes. As can be seen from comparison of TSD curves for pure and doped PS, presence of chromophores does not change much relaxation processes at sub-zero temperatures, only some quantitative effect is present. In general, the peaks in doped PS are more prominent proving that addition of chromophore allows to probe the relaxation processes in polymer matrix in more details. It is clear that even at low temperatures there is some preferential orientation of dyes induced by poling. Its relaxation, most probably, also contributes to appearance of depolarization current. Since γ peak is related to rotation of phenyl rings, its shift to higher temperatures in doped

PS shows that this motion is hindered by presence of dye molecules making relaxation reorientation more difficult. Increase of β peaks at −30 and −60 °C is in agreement with the reported data concerning responsibility of *b* processes for relaxation of poled order in PS/DR1 system [2]. Since both pure and doped samples are amorphous and the same electrodes have been used in both cases, the difference between ρ peaks in pure and doped PS can be attributed to the variance in space charge formation and relaxation due to presence of dye molecules. Augmentation of the peak in doped PS indicates that the introduction of the dye creates irregularities where charge carriers can be trapped. Shift of the peak to lower temperature shows that the charge is trapped deeper at additional irregularities than at ones already existing in pure PS.

3.2. AC dielectric spectroscopy. Measurements of the real and the imaginary parts in frequency domain have been performed on doped PS at constant temperatures from 30 to 130 °C. Results are shown in Fig. 2 and 3. The α relaxation is seen as well defined loss peaks at temperatures higher than T_g (Fig. 2). The same process corresponds also to decrease of the real part of dielectric constant (Fig. 3). The dielectric strength associated with this process is $\Delta\varepsilon = 0.02$—0.03 in pure PS, but $\Delta\varepsilon = 0.25$—0.27 in doped PS. Increase of ε″ at high frequencies and low temperatures can be considered as a low frequency part of β relaxation peak located out

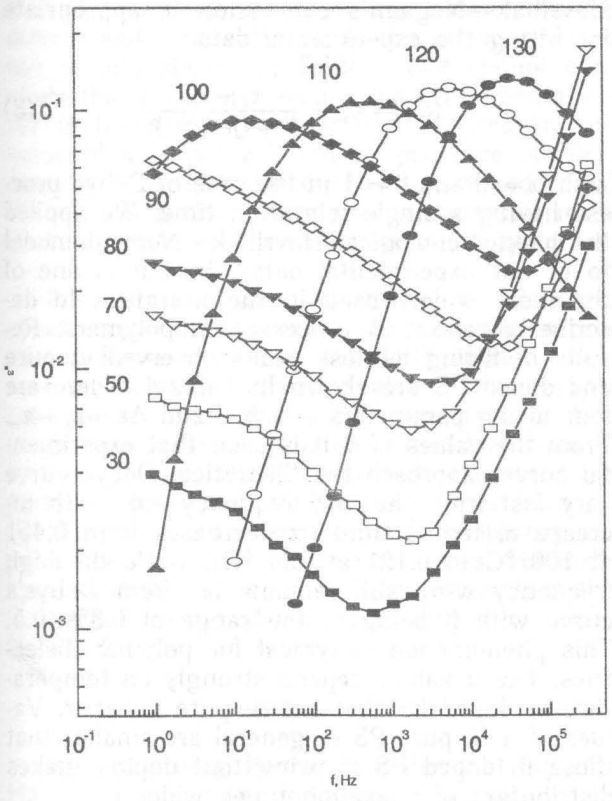

Fig. 2. The frequency dependence of the imaginary part of dielectric constant ε″(*f*) at different temperatures for PS/DR1 samples

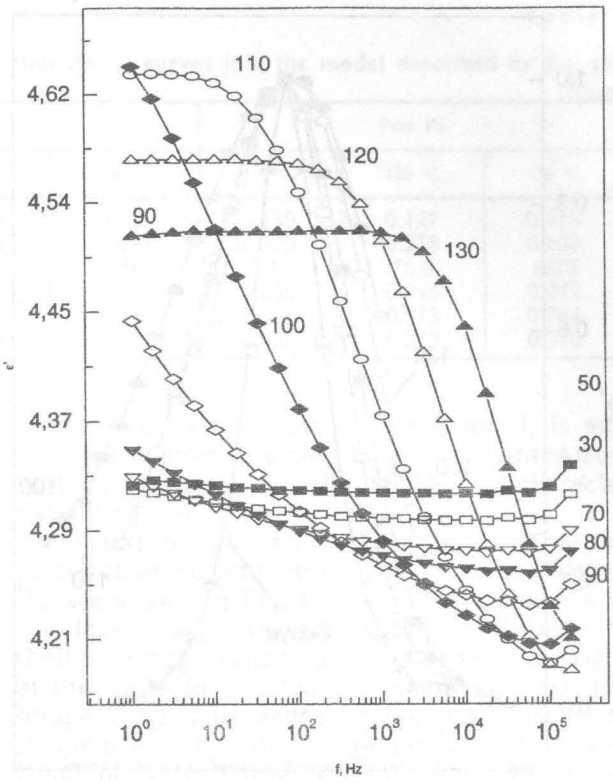

Fig. 3. The frequency dependence of the real part of dielectric constant ε′(*f*) at different temperatures for PS/DR1 samples

of the employed frequency range. Increase of ε″ with decreasing frequency for sub-T_g temperatures can be attributed to conductivity effect at low frequencies. As for the absolute values of ε′ the dielectric constant in doped PS is slightly higher than that in pure PS due to the effect of strongly polar dopant. Low frequency values of ε′ in the rubbery state of doped polymer decrease with temperature. This effect is probably caused by thermal expansion.

The loss peaks have been analyzed in more details and normalized curves are presented in Fig. 4 for doped samples together with theoretical Debye curve. As one can see, all experimental curves are much broader than the ideal one, indicating existence of a broad distribution of relaxation times. At the same time, a prominent narrowing of loss peak is observed with increase of temperature, therefore the peaks can not be scaled in a single master curve in contrast to the data reported earlier for the same system [3]. The reason is that the range of studied temperatures in our case was much wider comparing to that employed by Dhinojwala et al [3]. Contraction of loss peak with increase of temperature indicates that the distribution of relaxation times becomes narrower at high temperatures. This shows that PS/DR1 system is not thermoreologically simple, i. e. temperature-time superposition principle is not entirely applicable for this range of temperatures. This conclusion is in accordance with our previously reported data on comparison of isothermal and thermally stimulated processes in the same system and

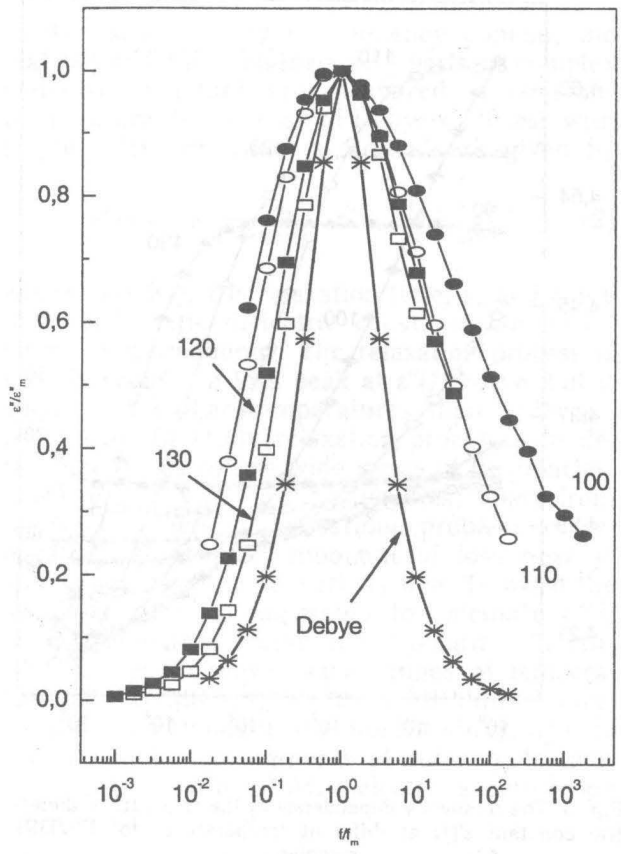

Fig. 4. The normalized frequency dependence of the imaginary part of dielectric constant ε''/e''_{max} at different temperatures for PS/DR1 samples and theoretical Debye curve

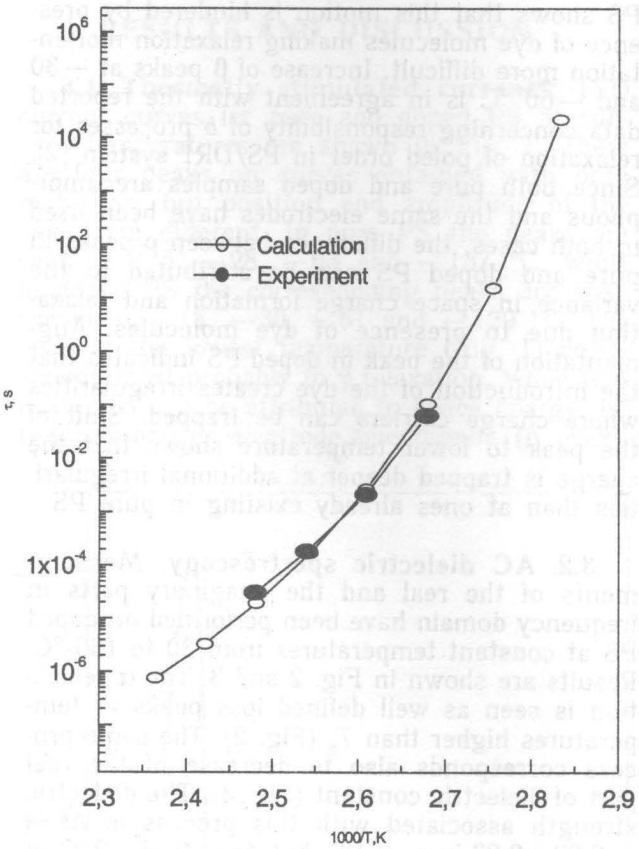

Fig. 5. The fitting of the experimentally obtained temperature dependence of relaxation times for PS/DR1 samples to theoretical WLF model

with the results presented by Dhinojwala et al [3] about increase of stretched exponential coefficient when fitting of experimental second harmonic generation decay to KWW equation has been attempted.

From the position of ε'' peaks one can find the temperature dependence of relaxation times in rubbery state of doped PS. It is shown in Fig. 5 that the experimental results for PS/DR1 can be appropriately fitted to WLF model represented by Eq. (1) and applicable for temperatures higher than T_g. Values of the fitting parameters ($\tau(T_g) = 200$ s, $C_1 = 15$, $C_2 = 50$ °C, $T_g = 86$ °C) appeared to be of the same order as those reported for PS doped with DR1 [3] ($\tau(T_g) = 200$—300 s, $C_1 = 15$, $C_2 = 40$ °C, $T_g = 94$ °C) and for PS doped with 4′(diakylamino)-4-(methylsulfonyl) azobenzene [5] ($\tau(T_g) = 27$ s, $C_1 = 11.6$, $C_2 = 46.3$ °C, $T_g = 91$ °C). Experimental points for pure PS do not correspond to WLF theoretical curve taking into account the above-mentioned parameters. The loss peaks for PS/DR1 at all studied temperatures are shifted to higher frequencies comparing to those for pure PS indicating that the relaxation time decreases with doping, as shown in Fig. 5, therefore the dopant has the definite plasticising effect.

As one can see from Fig. 2 and 4, the loss peaks for doped PS are asymmetrical in relation to peak frequency. For such a case, empirical Havriliak—Negami's expression is appropriate for fitting the experimental data

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} \qquad (3)$$

with $\alpha = 0$ and $\beta = 1$ in the case of Debye process having a single relaxation time. We applied the phenomenological Havriliak—Negami model to fit our experimental data, since it is one of the most widely used in the literature to describe α relaxation processes in polymers. Results of fitting for loss peaks observed in pure and doped PS are shown in Table 1. There are four fitting parameters — α, β, τ and $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$. From the values of α it is clear that experimental curves approach the theoretical Debye curve very fast from the low frequency side with increase of temperature (α decreases from 0.451 at 100 °C to 0.121 at 130 °C), while the high frequency wing still remains far from Debye's curve with β being in the range of 0.35—0.5. This phenomenon is typical for polymer dielectrics. The α values depend strongly on temperature in doped PS, but not in pure polymer. Values of α in pure PS in general are smaller that those in doped PS showing that doping makes distribution of relaxation times wider.

The dielectric strength $\Delta\varepsilon = 0.5$—0.57 in PS/DR1 is much higher then $\Delta\varepsilon = 0.04$—0.045 in pure polymer indicating that the increased

Table 1

Havriliak—Negami's parameters obtained by fitting experimental ε'' curves into the model described by Eq. (3)

Parameter	PS doped with DR1				Pure PS		
	100 °C	110 °C	120 °C	130 °C	110 °C	120 °C	130 °C
α	0.451	0.323	0.194	0.121	0.139	0.127	0.216
β	0.438	0.508	0.354	0.398	0.379	0.278	0.403
$\tau(s)$	3.87	184.7	1686	12800	3.81	75.9	1873
$\Delta\varepsilon$	0.573	0.505	0.548	0.504	0.039	0.045	0.042
$m=(1-\alpha)$	0.549	0.677	0.806	0.879	0.861	0.873	0.784
$n=\beta(1-\alpha)$	0.240	0.344	0.285	0.350	0.326	0.243	0.316

value of dielectric constant in doped PS at low frequencies in comparison with pure PS indeed results from the high dipole moment of chromophore molecules, while presence of the dye does not effect the value of dielectric constant at high frequencies. Within the experimental error the dielectric strength $\Delta\varepsilon$ shows no temperature dependence either in pure or in doped PS, but its value in both materials are two times higher than that obtained from $\varepsilon'(f)$ curves shown in Fig. 3.

It is generally assumed that the high frequency behavior is described by the peak shape coefficient $n=\beta(1-\alpha)$. It has been found by Koehler et al [4] that n remains constant at different temperatures in PS doped with 4'(diakylamino)-4-(methylsulfonyl) azobenzene and it was asserted that the shape of the high frequency wing arises from the jumpy reorientation of chromophores in their environment assuming that this process is entirely associated with the dopant and thus extrinsic to the polymer. From our results shown in Table 1 one cannot conclude that $n=$ const even if the experimental error is taken into consideration. Moreover, the value of n is not affected by presence of DR1, since it is of the same order for pure and doped PS indicating that in our case n correlates most probably with the polymer intrinsic dynamics.

3.3. Hamon's approximation. AC dielectric spectroscopy allowed us to study relaxation processes above T_g, while the TSD current measurements were performed at sub-zero temperatures. To cover the gap between these two ranges we performed Hamon's transformation of isothermal depolarization currents measured experimentally at different temperatures from 20 to 125 °C in order to obtain the frequency dependence of ε'' at these temperatures. Hamon's approximation is based on assumption that the isothermal current density response corresponds to von Schweidler equation

$$i(t)=i_0\cdot t^{-n}. \tag{4}$$

By performing Fourier transform of Eq. (4), Hamon obtained the following expression

$$\varepsilon''(f)=1.59\cdot t_c\frac{i(t_c)}{\varepsilon_0 E} \quad \text{with} \quad f=\frac{0.1}{t_c}, \tag{5}$$

where ε_0 is permittivity of free space, t_c is any moment of time t related to the isothermal current curve $i(t)$, E is poling field, f is characteristic frequency.

Results of calculations based on original depolarization current curves for pure and doped PS are shown in Fig. 6. To facilitate analysis of the loss peaks, we normalized amplitudes to their maximum values. In order to see the origin of the relaxation related to Hamon's curves, the temperature dependence of the particular peak frequencies are plotted together with the corresponding dependencies experimentally measured by AC dielectric spectroscopy. The data presented in Fig. 7 show that two points, at 80 °C for pure PS and at 90 °C for PS/DR1, are in qualitative agreement with AC dielectric spectrosco-

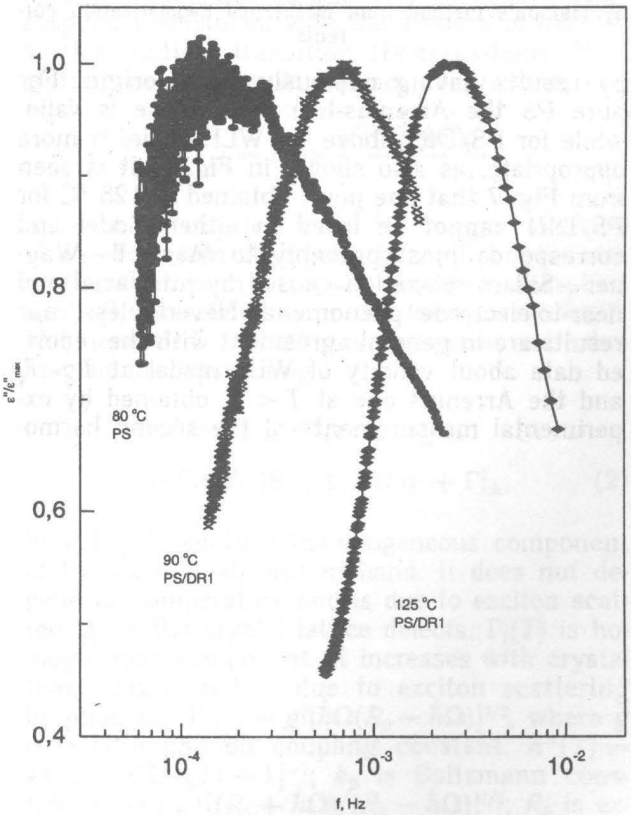

Fig. 6. The normalized frequency dependence of the imaginary part of dielectric constant $\varepsilon''/\varepsilon''_{max}$ for PS/DR1 and PS samples at different temperatures calculated according to Hamon's approximation from isothermal depolarization currents

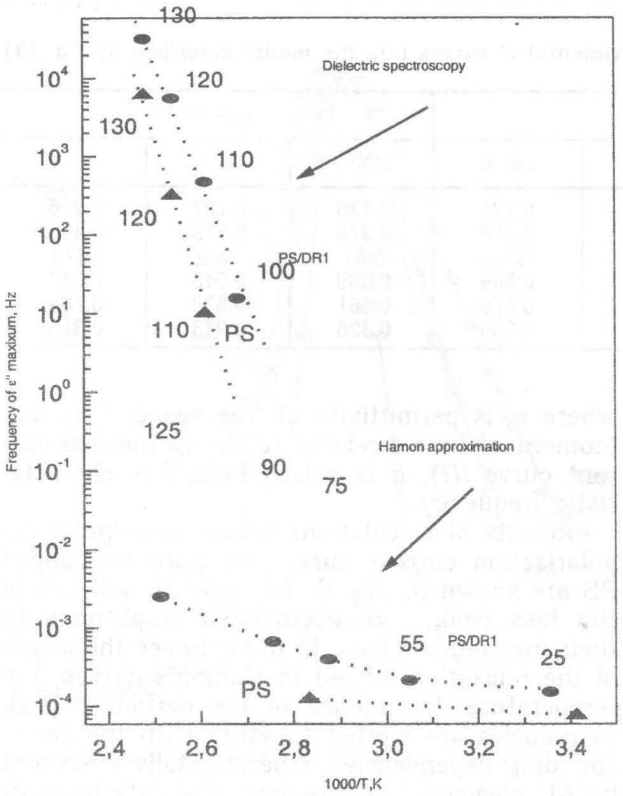

Fig. 7. Experimentally obtained temperature dependence of the frequency corresponded to a maximum of ε″ peak for PS/DR1 and PS from the results of AC dielectric spectroscopy supplemented with the corresponding data obtained by Hamon's method from isothermal depolarization currents

py results having obviously the a origin. For pure PS the Arrenius-like dependence is valid, while for PS/DR1 above T_g, WLF model is more appropriate, as also shown in Fig. 5. It is seen from Fig. 7 that one point obtained at 125 °C for PS/DR1 cannot be fitted in either model and corresponds most probably to Maxwell—Wagner—Sillars relaxation caused by interfacial and near-to-electrode phenomena. Nevertheless, our results are in general agreement with the reported data about validity of WLF model at $T > T_g$ and the Arrenius one at $T < T_g$ obtained by experimental measurements of the second harmonic generation decay at different temperatures in doped PS [3].

4. SUMMARY AND CONCLUSIONS

The dielectric behavior of pure and doped PS has been studied and compared. Apart from conventional AC dielectric spectroscopy in the frequency domain we used TSD current measurements at sub-zero temperatures and Hamon's transformation of isothermal depolarization currents in order to extend the ranges of studied temperatures and frequencies and to probe not only a relaxation, but also other processes characteristic for temperatures lower than T_g. It has been shown that presence of DR1 chromophore molecules affects a relaxation behavior of a host polymer in such a way that the distribution of relaxation times becomes wider, the dielectric constant and the dielectric strength increases and the dopant (DR1) shows a definite plasticising effect. It has been found that PS/DR1 system is not a thermoreologically simple one, so that the temperature-time superposition principle is not applicable for $T>T_g$. At infra-low frequencies and at sub-zero temperatures, the b relaxation comes out. Although the b processes are similar both in pure and doped PS, nevertheless some quantitative difference has been detected. The corresponding TSD and loss peaks in PS/DR1 samples were more prominent than in pure PS. It is probable therefore that the b processes in PS influence relaxation behavior of the chromophore molecules at sub-T_g temperatures.

References

1. *Ghebremichael F., Kuzyk M. G.* and Lackritz H. S. // Prog. Polym. Sci. 22, 1147 (1997).

2. *Schen M. A., Mopsik F. I.* Nonlinear Optical Properties of Organic Materials IV, SPIE 1560 (Int. Soc. Opt. Eng. Washington, 1999).

3. *Dhinojwala A., Wong G. K., Torkelson J. N.* // J. Chem. Phys. 100, 6046 (1994).

4. *Koehler W., Robello D. R., Willard C. S., Williams D. J.* // Macromolecules 34, 4589 (2001).

5. *Fedosov S., Giacometti J. A., Leal Ferreira G. F., Costa M. M.* // J. Appl. Phys. 82, 4355 (1997).