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RELAXATION PROCESSES IN NONLINEAR OPTICAL POLYMER FILMS

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Dielectric properties of the guest-host polystyrene/DR1 system have been studied by the AC dielectric spectroscopy method at frequencies from 1 Hz to 0,5 MHz and by the thermally stimulated depolarization current (TSDC) method from – 160 to 0 °C. The relaxation peaks at infra-low frequencies from 10^{-5} to 10^{-2} Hz were also calculated using the Hamon's approximation. Three relaxation processes, namely, α , β and δ ones were identified from the TSDC peaks, while the $\varepsilon''(f)$ dependence showed a non-Debye ρ -peak narrowing with temperature. The activation energy of the α -relaxation appeared to be 2,57 eV, while that of the γ -process was 0,52 eV. Temperature dependence of the relaxation time is agreed with the Williams-Landel-Ferry model. The $\varepsilon''(f)$ peaks were fitted to Havriliak-Negami's expression and the corresponding distribution parameters were obtained.

Keywords: POLYSTYRENE, DR1, NONLINEAR OPTICAL POLYMERS, AC DIELECTRIC SPECTROSCOPY.

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1. INTRODUCTION

Nonlinear optical polymers with huge chromophore molecules embedded in a polymer matrix have prospects of wide application in modern optical devices for the second harmonic generation (SHG), the optical parametric amplification (OPA), the optical rectification (OR), etc. [1, 2], therefore their stability and relaxation behavior are of the great practical and theoretical interest.

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

In this paper we study a system obtained by doping atactic polystyrene (PS) with disperse red 1 (DR1) dye molecules. Main transitions in PS are well established [3]. The α -process is the glass-rubber transition observed near T_g temperature. The β -transition is seen at sub- T_g temperatures from – 10 to + 60 °C, while γ and δ are cryogenic transitions at – 120 and – 230 °C

correspondingly. The objective of this study was to find how doping affects the relaxation processes in PS.

In the case of the AC dielectric spectroscopy in the frequency domain, a relaxation process is seen as a peak at the $\varepsilon''(f)$ curve [1]. To probe the range of infra-low frequencies, Hamon [4] suggested a procedure for calculating the $\varepsilon''(f)$ dependence from isothermal depolarization current curves. Valuable information about relaxation processes can be obtained also from analysis of the thermally stimulated depolarization (TSD) current peaks [5]. All three methods were used in the present study. The AC experiments at $T > T_g$ were supplemented by the TSD current measurements at sub-zero temperatures and by Hamon's transformation of isothermal currents in the range of 20 ÷ 125 °C. Thus, the temperature range from -160 to +130 °C and the frequency range from 10^{-5} to 10^{-6} Hz were productively covered.

2. EXPERIMENTAL SETUPS

Atactic amorphous PS ($M = 250\ 000$) was obtained by purification of a commercial resin. The 20 μm -thick samples with 2% of dye molecules were prepared from a mixture of PS and DR1 dissolved in chloroform. It has been found by the x-ray diffraction method that the polymer films were entirely amorphous with the glass transition temperature of $T_g = 95$ °C. Aluminum electrodes of 2 cm^2 area were deposited on both surfaces of the sample by the thermal evaporation in vacuum. The AC measurements were performed by sweeping the frequency range from 1 Hz to 0.5 MHz at constant temperatures from 90 to 130 °C, while the $\varepsilon''(f)$ and $\varepsilon'(f)$ dependencies were measured by the impedance analyzer.

For TSD measurements, the samples were clamped between two electrodes and poled at 300 V for 10 min. Then the samples were cooled to -160 °C by immersing them in liquid nitrogen with the poling field still applied. The films were reheated at the rate of 3.5 °C·min⁻¹ and the depolarization current was measured. Isothermal currents at constant temperatures from 20 to 125 °C for Hamon's transformation were measured after short circuiting of the samples poled isothermally for about 10^4 s at 200 V. There were four peaks on TSD curves (not shown here). In pure PS, the peaks were seen at -5, -28, -63 and -137 °C, while in doped PS the corresponding peaks were at -15, -30, -61 and -129 °C. Our results for pure PS were in agreement with those presented in [6], the difference can be accounted for different molecular mass and the heating rate. The peak at the lowest temperature was attributed to the γ -relaxation, while the peak near 0 °C was probably caused by the space charge, interfacial and/or electrode processes (ρ -peak). The origin of the peaks around -30 and -60 °C was not clear, but they were probably related to β -processes. Doping did not change much relaxation processes at sub-zero temperatures, only some quantitative effect was present. Increase of β -peaks at -30 and -60 °C was in agreement with the reported data about partial responsibility of the β -relaxation for the poled order in the PS/DR1 system [7].

Real and imaginary parts of the dielectric constant in the frequency domain have been measured for doped PS at constant temperatures from 30 to 130 °C (Fig. 1). The α -relaxation was seen as well defined loss peaks at

$T > T_g$. No much information can be obtained about behavior below T_g . Increase of ε'' with decreasing frequency for sub- T_g temperatures can be attributed either to the conductivity effect at low frequencies, or to be considered as a high frequency part of the β -relaxation peaks positioned out of the employed frequency range.

The loss peaks were analyzed in more details. It has been found that all curves were much broader than the ideal Debye curve, indicating existence of a broad distribution of relaxation times. Narrowing of the loss peak with temperature showed that the distribution also becomes narrower indicating that the PS/DR1 system is not thermorheologically simple [8], i.e. the temperature-time superposition principle is not entirely valid for this range of temperatures. This conclusion is in accord with the previously reported data on comparison of isothermal and thermally stimulated processes in this system [9] and with results presented in [10] about increase of the stretched exponential coefficient while fitting the experimental second harmonic generation decay to the KWW (Kohlrausch-Williams-Watts) equation.

From position of the peaks in Fig. 1 one can find the temperature dependence of relaxation times in the rubber state. The experimental results were well fitted to the WLF (Williams-Landell-Ferry) model applicable for $T > T_g$. The 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 previously for doped PS [10, 11].

As one can see from Fig. 1, the loss peaks are not symmetrical. For such a case, an empirical Havriliak-Negami's model is appropriate for fitting the experimental data [12].

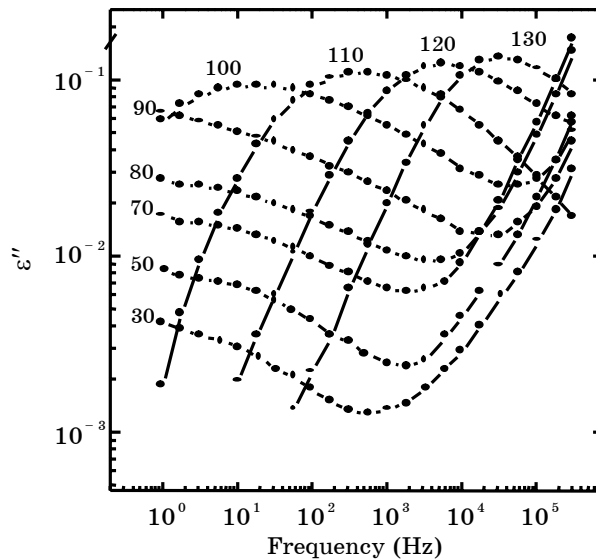


Fig. 1 – Frequency dependence of the imaginary part of the dielectric constant in doped PS at different temperatures.

There were four fitting parameters, namely α , β , τ and $\Delta\varepsilon = \varepsilon_s - \varepsilon_{dc}$. From values of the α coefficient it was clear that with increase of temperature, the experimental curves approach the theoretical Debye curve from the low frequency side, while the high frequency side remains far from the ideal curve. Values of α in pure PS were smaller than those in doped PS showing that the doping makes distribution of relaxation times wider. The dielectric strength $\Delta\varepsilon = 0.5 \div 0.57$ in doped PS was much higher than $\Delta\varepsilon = 0.04 \div 0.045$ in pure polymer indicating that the increased value of the dielectric constant in doped PS at low frequencies in comparison with pure PS indeed resulted from the high dipole moment of the chromophore molecules, while presence of the dye does not affect the value of the dielectric constant at high frequencies.

The 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 temperature ranges, we performed Hamon's transformation of the isothermal currents [8] 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 is close to von Schweidler's equation $i = i_0 t^{-n}$. This dependence was actually observed in our experiments. The results of calculations are shown in Fig. 2. To facilitate analysis of the loss peaks, their amplitudes were normalized.

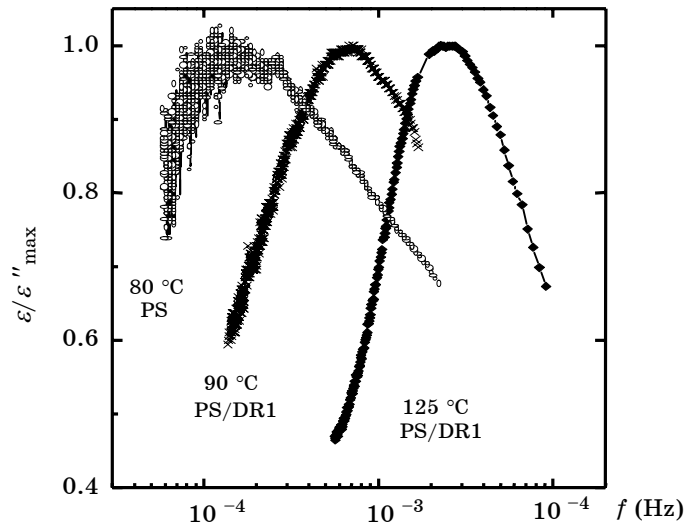


Fig. 2 – Normalized loss peaks in doped PS at different temperatures calculated from isothermal depolarization currents using Hamon's approximation

It has been found that the peaks at all studied temperatures were shifted to higher frequencies comparing to those for pure PS (not shown here) and indicating that the relaxation time decreases with doping, so the dopant has a definite plasticizing effect to the relaxation process characterized by the loss curves. In order to see the origin of this relaxation, we plotted the temperature dependence of the characteristic peak frequencies for the curves obtained by Hamon's approximation together with those measured by the AC spectroscopy.

Results presented in Fig. 3 show that the two curves cannot be both fitted in one model. The α -origin of the high temperature peaks is clear. As for the Hamon peaks, they originate most probably from the β -relaxation. The $f_c(T)$ dependence at sub- T_g temperatures is close to the Arrhenius formula with the activation energy of 0.52 eV, while the WLF model is more appropriate above T_g . Our results are in agreement with the reported data on the same system, particularly with the conclusion made in [9] about efficiency of β -relaxation processes and with the data [10] proving validity of the WLF model at $T > T_g$ and the Arrhenius model at $T < T_g$ obtained by measurements of the second harmonic generation signal decay at different temperatures. The activation energy was of the same order as that reported for β - and γ -processes [6, 9].

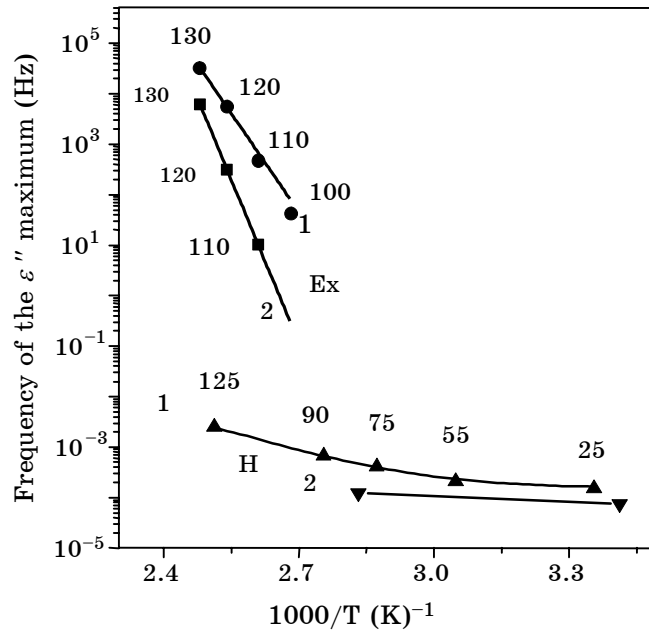


Fig. 3 – Dependence of the experimentally measured (*Ex*) and calculated by Hamon's method (*H*) frequency corresponded to the maximum of the dielectric losses of the PS/DR1 samples (1) and pure PS (2) at different temperatures (shown by figures near curves). Results of calculations by Arrhenius formula are shown by solid lines.

3. FINAL REMARKS

The dielectric behavior of pure and doped PS has been studied and compared. Apart from conventional AC dielectric spectroscopy in a 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 the α -relaxation, but also other processes characteristic for temperatures lower than T_g . It has been shown that presence of DR1 chromophore molecules affects the α -relaxation behavior of

the 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 plasticizing effect. It has been found that the 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 β -relaxation appears. Although the β - processes are similar in both pure and doped PS, nevertheless some quantitative difference has been detected. The corresponding TSDC and loss peaks in PS/DR1 samples were more prominent than in pure PS. It is probable therefore that the β -processes in PS influence relaxation behavior of the chromophore molecules at sub- T_g temperatures. The data can be used for estimation of thermal and temporal stability of polarization in NLO polymers.

РЕЛАКСАЦІЙНІ ПРОЦЕСИ В НЕЛІНІЙНИХ ОПТИЧНИХ ПОЛІМЕРНИХ ПЛІВКАХ

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Діелектричні властивості систем полістирол-хромофор DR1, зв'язаних по типу «гість-господар» були вивчені методом діелектричної спектроскопії на частотах від 1 Гц до 0,5 МГц та методом термостимульованої деполяризації в діапазоні температур від -160 до 0 °С. Релаксаційні піки на інфранизких частотах в діапазоні від 10^{-5} до 10^{-2} Гц були також розраховані у наближенні Хамона. Три релаксаційних процеси, а саме: α , β та δ були виявлені з піків термостимульованої деполяризації, в той час коли залежність $\varepsilon''(f)$ має недебаєвський ρ -пік, який звужується з температурою. Знайдена енергія активації для α -релаксації, яка дорівнює 2,57 еВ, у той самий час, коли для γ -процесу вона складає 0,52 еВ. Температурна залежність часу релаксації добре узгоджується з моделлю Вільямса-Ланделла-Феррі. Піки залежності $\varepsilon''(f)$ співпадають з результатами, обчисленими за допомогою співвідношення Гавриляка-Негамі. Були одержані відповідні характеристики розподілу.

Ключові слова: ПОЛІСТИРОЛ, ХРОМОФОР DR1, НЕЛІНІЙНІ ОПТИЧНІ ПОЛІМЕРИ, ДІЕЛЕКТРИЧНА СПЕКТРОСКОПІЯ.

РЕЛАКСАЦИОННЫЕ ПРОЦЕССЫ В НЕЛИНЕЙНЫХ ОПТИЧЕСКИХ ПОЛИМЕРНЫХ ПЛЕНКАХ

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Диэлектрические свойства систем полистирол-хромофор DR1, связанных по типу «гость-хозяин», были изучены методом диэлектрической спектроскопии

на частотах от 1 Гц до 0,5 МГц и методом термостимулированной деполяризации в диапазоне температур от -160 до 0 °С. Релаксационные пики на инфранизких частотах в диапазоне от 10^{-5} до 10^{-2} Гц были также рассчитаны в приближении Хамона. Три релаксационных процесса, а именно: α , β и δ были выявлены из пиков термостимулированной деполяризации, в то время как зависимость $\varepsilon''(f)$ имеет недебаевский ρ -пик, который сужается с температурой. Найдена энергия активации для α -релаксации, которая имеет величину 2,57 эВ, в то время как для γ -процесса она составляет 0,52 эВ. Температурная зависимость времени релаксации хорошо согласуется с моделью Вильямса-Ланделла-Ферри. Пики зависимости $\varepsilon''(f)$ совпадают с результатами, полученными с помощью соотношения Гавриляка-Негами. Соответствующие характеристики распределения были получены.

Ключевые слова: ПОЛИСТИРОЛ, ХРОМОФОР DR1, НЕЛИНЕЙНЫЕ ОПТИЧЕСКИЕ ПОЛИМЕРЫ, ДИЭЛЕКТРИЧЕСКАЯ СПЕКТРОСКОПИЯ.

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