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Dielectric Relaxation in Poly(2-Ethynylnaphtalene) Determined by Thermally Stimulated Depolarization Currents

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Summary. The thermally stimulated depolarization currents from poly(2-ethynylnaphtalene) with cis-cisoidal and trans-cisoidal structures were studied over the temperature range 200-380 K. The single peak ρ of the cis-cisoidal isomer was assigned to the Maxwell-Wagner polarization. The β_1 and β_2 peaks of the trans-cisoidal isomer arise from a single dipolar relaxation process and respectively from a dipolar relaxation distributed in natural frequency. Certains assignements are based on comparative work on polyphenylacetylene.

Introduction. In recent years, the novel electric properties observed in polyacetylene (SHIRAKAWA, et al.,1977; CHIANG, et al.,1977; CHIANG, et al.,1978) have determined an increasing amount of interest in a number of its analogs (DIACONU, DUMITRESCU,1979; DIACONU, DUMITRESCU,1980a; DIACONU, DUMITRESCU,1980b; DIACONU, et. al.,1981; DEITS, et al.,1981; CUKOR, et al.,1981). First detailed results concerning the dielectric relaxation in analogs of polyacetylene were reported on polyphenylacetylene (PPA) (DIACONU, DUMITRESCU,1982) using thermally stimulated depolarization current (TSDC) technique. Complex relaxation spectra were observed in this polymer. The complexity of the spectra and the origin of the constituent relaxation processes depend on the isomeric structure of the polymer.
This paper will analyse the TSDC data obtained on poly(2-ethynylnaphtalene) (P2EN) having cis-cisoidal and trans-cisoidal structures.

Experimental. The investigated polymers had respectively cis-cisoidal (60% crystallinity) and trans-cisoidal (amorphous) structures (SIMIONESCU, et al., 1976). Measurements were carried out on disc-shaped samples (Ø = 13 mm) in dry N_2 or O_2 at normal pressure, using the chamber presented elsewere (DIACONU, DUMITRESCU,1978). The discs were provided with vacuum evaporated gold electrodes of circular form (Ø = 10 mm) centrally placed on both sides of the disc.
The thermal cycles of polarization and depolarization of samples consisted of the following steps: a sample with a polarization field E_p was warmed up to the polarization temperature T_p, which was maintained constant for a polarization

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time t_p; after cooling to 200 K using liquid nitrogen, E_p was removed and the sample was short-circuited for 10 min in order to eliminate the rapid depolarization currents; then the depolarization currents were recorded at a heating rate of 5 K/min.

Results and discussion. The TSDC spectra of the isomers of P2EN are presented in Fig.1. The cis-cisoidal (c-c) polymer consists of one high and broad peak ρ whereas cis-transoidal (c-t) isomer exibits two smaller peaks β_1 and β_2. However, the ρ peak was already evidenced by transient current technique (DIACONU, DUMITRESCU,1980b) and was attributed to the Maxwell-Wagner polarization. That assignment is now supported by the TSDC results, since the ρ peak is much higher than those corresponding to the amorphous isomer.

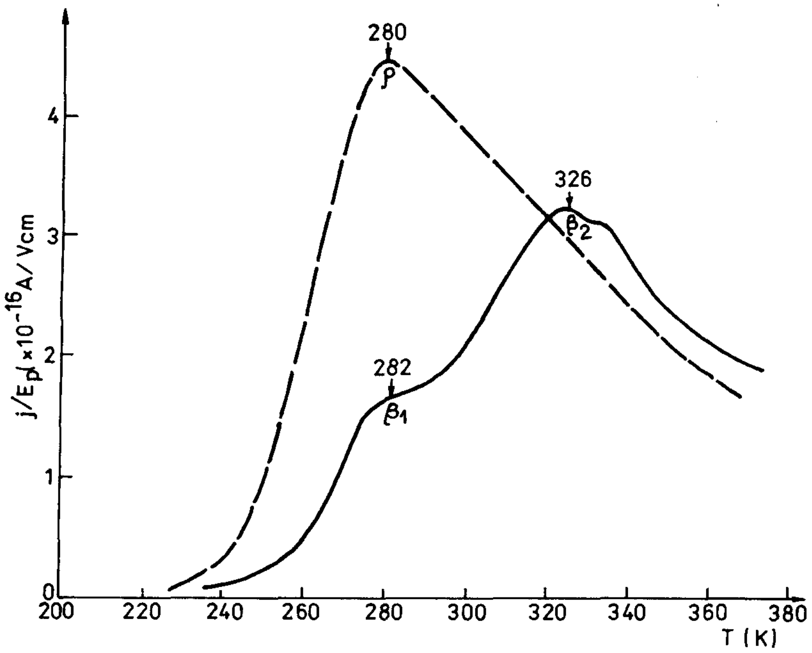

Fig.1. TSDC spectra of P2EN. Polarizing condition: T_p = 370 K; E_p = 32,2 V/cm; t_p = 30 min

It was previously found that the TSDC thermograms of PPA (trans-cisoidal isomer) consists of two well separated peaks, β_1 (225 K) and β_2 (346 K), originating from a single dipolar process and respectively from a dipolar relaxation process distributed in natural frequency. The similarity between the structures of these two polymers may suggest that the relaxation processes observed in $P2EN_{t-c}$ could have the same origins assigned to the corresponding processes in PPA. Indeed, the dependence of the maximum current of the β_1 and

β_2 peaks on the polarizing field was found to vary linearly through the origin, similarily to PPA_{t-c}, supporting the dipolar origin of these processes. The activation energies determined using both the initial current rise method (IC) applied to the thermograms obtained by partial heating of the electrets and the Bucci-Fieshi-Guidi's method (BFG) (BUCCI, et al.,1966) for the entire cleaned peak are presented in table 1. The relaxation strength and the dipole moment per structural unit, determined using a method presented elsewhere (DIACONU, DUMITRESCU,1978), are also shown.

TABLE 1

The relaxation characteristics of P2EN

Polymer	Peak	T_m (K)	Activation energy E(eV)		$(\varepsilon_s - \varepsilon_\infty)$ x)	μ(D)
			IC	BFG		
$P2EN_{c-c}$	ρ	280	0.60	0.62	1.8×10^{-1}	-
$P2EN_{t-c}$	β_1	282	0.51	0.51	1.1×10^{-1}	1.1
	β_2	326	1.49	1.32	2.0×10^{-1}	1.7

x) ε_s and ε_∞ are static and optical frequency dielectric constants

By partial depolarization of the electrets a single value of the activation energy was found for both β peaks. Futher was carried out a comparison of the theoretical Debye relaxation curves, obtained according to a method employed previously (DIACONU, et al.,1980), and experimental curves derived from the cleaned peaks. A good agreement between these two kinds of curve was found only for the β_1 peak (Fig.2). The findings above support that the β_1 peak arises from a single relaxation process, whereas the β_2 peak from a distributed relaxation process. Since a distribution in activation energy is ruled out, a distribution in natural frequency generates the distribution of the β_2 process.

The activation energies of the β_1 and β_2 relaxation processes (Table 1) are higher than those found for the corresponding peaks of PPA_{t-c} (DIACONU, DUMITRESCU,1982). This fact may be attributed to the higher dimension of the naphtalene side-group which generates higher interactions. It was previously concluded that β_1 and β_2 relaxations in PPA_{t-c} involves a combination of the phenyl ring motion coupled with the motion of the backbone chain. The backbone chain segments involved in the β_1 and β_2 peaks are of various lengths, longer segments for β_2 peak. These motions could be oscilation of the phenyl rings coupled with the wagging motion of the backbone chain (DIACONU, DUMITRESCU,1982).

Based on the similar structure of the PPA_{t-c} and $P2EN_{t-c}$, it may suggest that the molecular motions responsable for relaxations in PPA_{t-c} are also involved in $P2EN_{t-c}$.

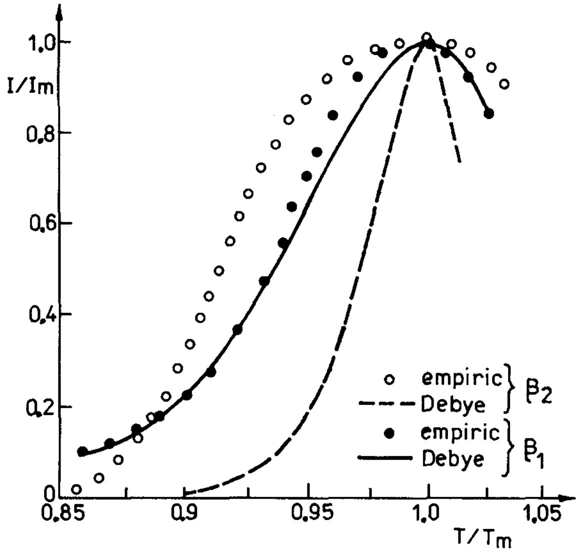

Fig.2. Comparison of theoretical and experimental relaxation curves for β_1 and β_2 peaks of $P2EN_{t-c}$

References.

1. BUCCI C., FIESHI R. and GUIDI G., Phys.Rev., 148, 816(1966)
2. CHIANG C.K., FINCHER C.R.Jr., PARK Y.W., HEEGER A.J., SHIRAKAWA H., LOUIS E.J., GAU S.C. and MacDIARMID A.G., Phys.Rev.Lett., 39, 1098 (1977)
3. CHIANG C.K., DRUY M.A., GAU S.C., HEEGER A.J., SHIRAKAWA A.H., LOUIS E.J., MacDIARMID A.G. and PARK Y.W., J.Am. Chem.Soc., 100, 1013 (1978)
4. CUKOR P., KRUGLER I. and RUBNER M., Macromol.Chem.Phys., 182, 165 (1981)
5. DEITS W., CUKOR P., RUBNER M. and JOPSON H., Polym.Prep., 22, 197 (1981)
6. DIACONU I. and DUMITRESCU Sv., Eur.Polym.J., 14, 971 (1978)
7. DIACONU I. and DUMITRESCU Sv., Eur.Polym.J., 15, 1155 (1979)
8. DIACONU I. and DUMITRESCU Sv., Eur.Polym.J., 16, 511 (1980)a
9. DIACONU I. and DUMITRESCU Sv., Bul.Inst.Politeh.Iaşi, Secţia II, XXVI, 63 (1980)b
10. DIACONU I., DUMITRESCU Sv. and SIMIONESCU Cr., Eur.Polym. J., 16, 515 (1980)
11. DIACONU I., DUMITRESCU Sv. and SIMIONESCU Cr., Polym. Bul., 4, 535 (1981)
12. DIACONU I. and DUMITRESCU Sv., J.Macromol.Sci.-Phys., 21, 555 (1982)
13. SIMIONESCU Cr., DUMITRESCU Sv., PERCEC V., Polym.J., 8, 139 (1976)

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