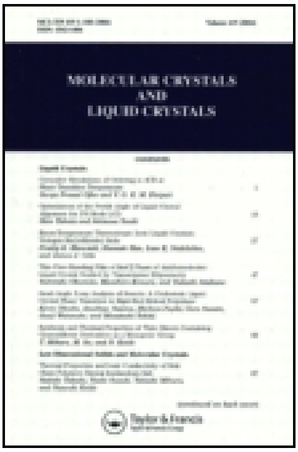

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DIELECTRIC RELAXATION PHENOMENA IN BUTADIENE-ACRYLONITRILE COPOLYMERS

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Abstract The polarization phenomena of the polybutadiene - acrylonitrile (PBAN) copolymers have been investigated in the vicinity of the glass transition region by methods of thermally stimulated depolarization currents (TSDC), thermally stimulated polarization currents (TSPC) and dc conductivity. Relaxation regions above the glass transition temperature Tg have been analyzed by thermal sampling and partial depolarization techniques in more detail. The effects associated with the cyclizing after pyrolysis in PBAN copolymers have been studied by thermally stimulated and viscoelastic measurements.

INTRODUCTION

Considerable effort has been directed towards understanding the electrical and optical properties of molecular solids built of conjugated molecules[1]. Recently, much interest has also been given to ladder polymers in which the π-electron conjugation is not limited to a single carbon chain but occurs in a ladder-like structure[2]. The conjugated π-electron polymeric systems hold much promise for explanation of the new conduction mechanism and of the high optical nonlinearity[3]. Both effects can be employed in photonic devices. The performed relaxation and polarization measurements are used for study of the ladder structure of PBAN copolymers.

EXPERIMENTAL

The commercial statistical polybutadiene-acrylonitrile (PBAN) copolymers (content 28% acrylonitrile), manufactured by Bayern AG, Germany, (M_w= 140,000; 240,000; and 400,000) have been choosed for this study. The glass transition temperatures T_g were determined by DTA measurements (Netzsch 404 T) with a heating rate of 4K/min. Amorphous PBAN samples (1 mm thick pellets) were prepared by molding-compression at 400 K for the thermally stimulated measurements. Thin films were casted by spin-coating of the viscous PBAN copolymer solution in dimethylformamide on glass or Si substrate, respectively.

All samples have been measured in unpyrolyzed and pyrolyzed modifications. Pyrolyzed polymer was obtained by pyrolysis of acrylonitrile comonomers. The pyrolysis leads to ring closure by the nitrile side group in the acrylonitrile comonomer, resulting in a ladder structure (Figure 1). The pyrolysis was induced by heating the copolymers at 225°C.

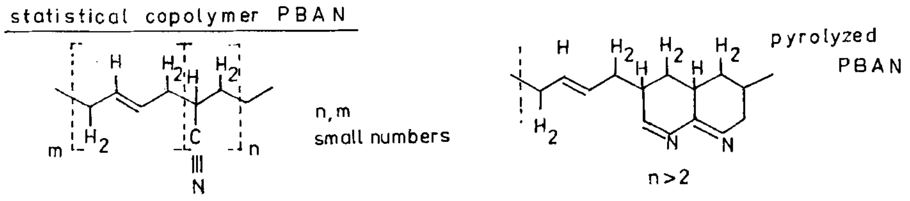
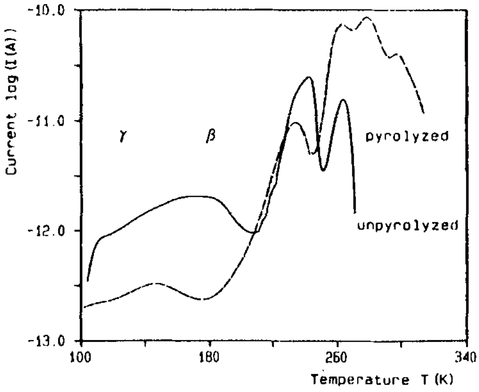


FIGURE 1 Schematic description of the PBAN modifications.

The TSDC and TSPC measurements were carried out in a set-up described previously[4]. The partial heating[5] (PH), and thermal sampling[6] (TS), techniques were used to investigate the multiplicity (overlapping) of TSDC peaks.

RESULTS AND DISCUSSION

Typical TSDC spectra of unpyrolyzed and pyrolyzed PBAN copolymers are given in Figure 2. The broad dispersion zone in the low-temperature region (LTR) is observed in unpyrolyzed and some pyrolyzed samples. In agreement with Furakawa,[7] we describe this broad low-temperature dispersion as composed of local β and γ relaxations.



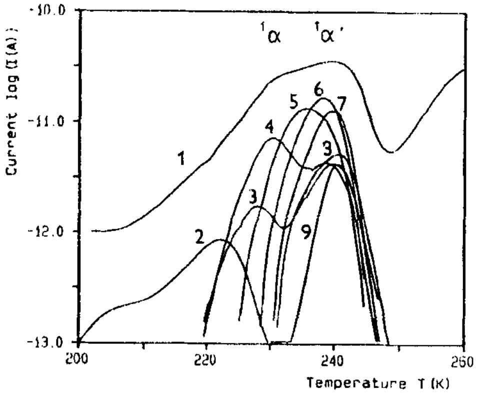
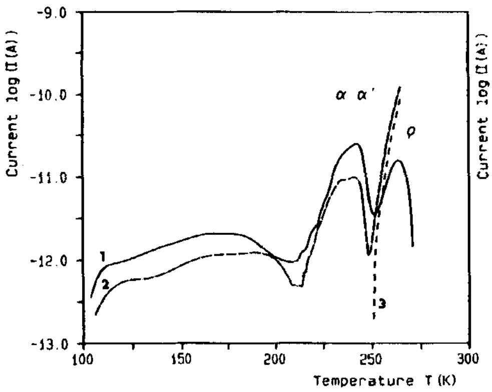


FIGURE 2 (left) TSDC spectra of PBAN modified copolymers. Polarization temperatures, T_p = 265 K (300 K), polarization electric fields, E_p= 10^6 V/m (3.10^5 V/m), polarization times, t_p= 900s (900s) for unpyrolyzed (pyrolyzed) samples.

FIGURE 3 Thermal sampling of unpyrolyzed PBAN copolymer (sampling window T_p-T_d= 3 K, E_p= 10^6 V/m, t_p= 900 s).

The differences of the TSDC curves of unpyrolyzed and pyrolyzed samples in the high temperature region (HTR) are as follows: In the unpyrolyzed samples, the dipolar TSDC peak at 230-242 K in the HTR is due to molecular mobility released at the glass transition temperature, T_g, of the copolymer. This interpretation is supported by our DTA measurements giving T_g= 232 K. The analysis of the dipolar α peak by the (TS) and (PH) techniques shows the broad distributions both in relaxation times (Figure 3) and in activation energies, W, (Table I). It is expected for polymers in the main transition region. The high resolution power of TS (sampling window 3 K), makes in some samples possible the decomposition another TSDC relaxation peak $^1\alpha'$ (T_m = 240 K) from the TSDC glass transition peak $^1\alpha$. This

$^1\alpha'$ peak is characterized by nearly single activation energy (W = 1.5 eV) and single relaxation time. We suppose to attribute this peak to the structural inhomogenities in the samples. The relaxation peak $^1\rho$ at the highest temperature (T_m= 261K, W = 1.5 eV) is due to a space-charge relaxation. This interpretation is supported by the fact that the peak is located at those temperatures at which an apparent dc conductivity of the sample occurs (Figure 4).



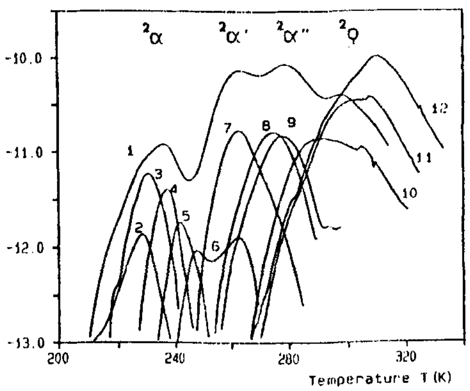


FIGURE 4 (left) Thermally stimulated phenomena in PBAN. TSDC (1) TSPC (2), dc conductivity (3).

FIGURE 5 Thermal sampling of pyrolyzed PBAN. $T_p - T_d = 3$ K, starting at 218 K, $E_p = 3.10^5$ V/m.

The pyrolysis of PBAN copolymers significantly changes the shape of TSDC spectrum in HTR (Figure 2). The dipolar TSDC $^2\alpha$-peak (glass transition peak) is slightly shifted towards higher temperature. The TH and PH techniques again show that the peak is distributed both in relaxation times (Figure 5) and in activation energies (Table I). The above mentioned peak denoted $^2\alpha'$ is shifted to higher temperature 263 K (W = 1.6 eV). Two other peaks ($^2\alpha''$ and $^2\rho$) are seen in Figures 2 and 5. The $^2\alpha'$, $^2\alpha''$, and $^2\rho$ processes partially overlap. The peak $^2\rho$ at the highest temperature (T_m = 298 K, W = 1.6 eV) we attribute to space-charge relaxation, according to same reasons as in unpyrolyzed sample (compare Figures 4 and 6). The origin of the middle peak $^{2}\alpha''$ (T_m = 279 K, W = 1.3 eV) with distribution of relaxation times (apparent from Figure 5), needs further investigation.

The magnitude of the non-Arrhenius type dc conductivity is lower in pyrolyzed samples (see Figure 6) than in the unpyrolyzed ones. In all samples, the observed dc conductivity sharply increases only at temperatures higher than are the temperatures of the $^{1}\alpha$ and $^{2}\alpha$ TSDC peaks (T_g regions). The evaluated parameters of TSDC relaxation processes and activation energies of dc conductivity are listed in Table I.

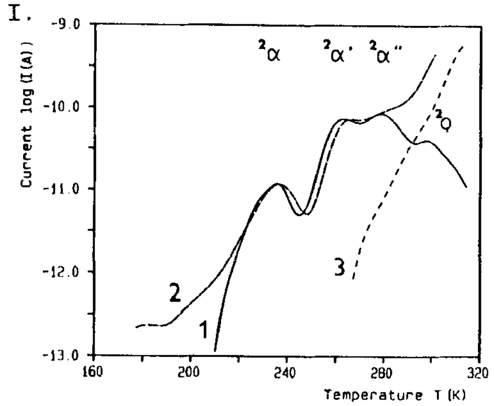


FIGURE 6 Thermally stimulated phenomena in pyrolyzed PBAN sample. TSDC (1), TSPC (2), dc conductivity (3).

TABLE I DC conductivity and relaxation parameters of PBAN.

sample	T [K]	W [eV],	log (τ_0[s]),	$E_{d.c.}$ [eV]
unpyrolyzed				
$^{1}\alpha$	232.4	0.9-1.2	-17.5 - (-24.2)	1.67
pyrolyzed				
$^{2}\alpha$	235.7	1.0-1.3	-19.5 - (-26.0)	1.25

The IR, UV-VIS and viscoelatic spectra were used to investigate the structural changes accompanying pyrolysis of the PBAN copolymers.

The results of the IR measurements are given in Figure 7. The typical peak at 2240 cm^{-1} assigned to the nitrile group (C = N) decreases while that of the imine bonds at 1650 cm^{-1}increases as the pyrolysis reaction (heating at 225 ^{o}C) proceeds (Figure 7a). The new peak appearing at 1650 cm^{-1} indicates the onset of polymer chain conjugation through the C=N bonds formation. Cyclizing of acrylonitrile groups (the presence of the conjugated imine system) introduces characteristic change in the optical absorption spectrum (Figure 7b).

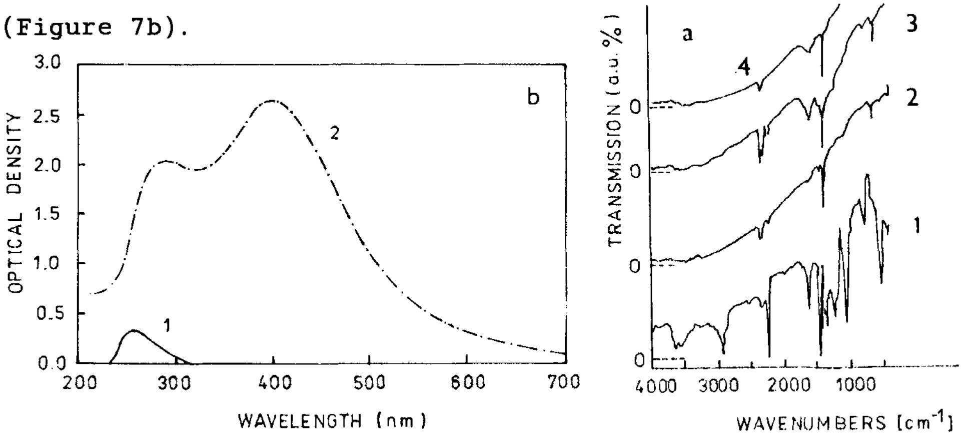


FIGURE 7 a) IR spectra PBAN before heating (curve 1), after achieving 225^{o}C (curve 2), heated at 225^{o}C for 60, 180 min (curves 3 and 4). b) UV-VIS absorption PBAN before pyrolysis (curve 1), pyrolyzed PBAN (curve 2)

The results of viscoelastic measurements are given in Figure 8. The creep curves (compliance D vs logarithmic time log t at various temperatures) of the pyrolyzed and unpyrolyzed sample are compared. The form of the both curve systems is similar; the absolute value of the comparable compliances are substantially lower in the pyrolyzed sample than in the unpyrolyzed one. The pyrolysis stiffers the chains and may increase the intermolecular cohesion forces. Both these effects lead to lower compliance in semicrystalline polymers. The decrease of mobility of the PBAN chains (the rubbery entrophic mobility is much reduced by energetic barriers hindering the free rotation in these chains) and possible crystalization is the plausible reason of the decrease of the pseudoequilibrium compliances with decreasing temperature. The time-temperature superposition principle[8] cannot be applied to none of the creep systems. The deviation from this - in rubbery polymers generally valid - principle indicates complex viscoelastic behaviour of the PBAN copolymers. The T_g creep jump is visible only at the low temperature creep curves (Figure 8). From this curves we may evaluate that T_g is close to 240 K both in the pyrolyzed and unpyrolyzed sample (if measuring time ~ 1s is taken).

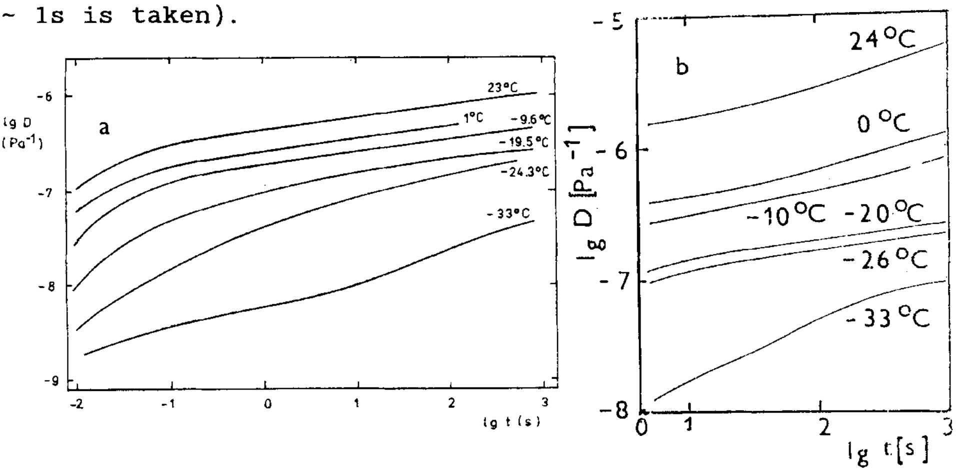


FIGURE 8 a),b) Creep curves at various temperatures pyrolyzed sample (a), unpyrolyzed sample (b).

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