

Thermal Depolarization Currents of Regenerated Cellulose Films

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Synopsis

The thermal depolarization current technique is applied to plasticized and unplasticized regenerated cellulose films. In unplasticized cellulose, two depolarization current bands are observed. The band with a current maximum occurring near 298°K (T_m), and with an activation energy, U , of 0.57 eV, is believed to be related to the second-order transition which is known to occur in dry cellulose in the vicinity of 298°K. The second band, with $T_m = 215^\circ\text{K}$ and $U = 0.26$ eV, is also present in the plasticized material, and possibly arises from primary hydroxyl group orientations. In cellulose films plasticized with glycerol, an intense band occurs at 271°K, with $U = 0.51$ eV, and is attributed to the plasticizer. A third band, occurring in the plasticized material near 300°K, has not been fully investigated.

INTRODUCTION

The thermal depolarization current technique of Bucci et al.^{1,2} is a method of investigating the dielectric properties of solids. In particular, it offers a means of studying the response of polar groups to an applied static electric field. This technique has been used to investigate a number of polymer systems.³⁻⁷ Because of the polar hydroxyl side groups in cellulose, this method should be suited for investigation of the cellulose system. This paper presents some preliminary results of depolarization current measurements in plasticized and unplasticized regenerated cellulose films.

EXPERIMENTAL

The material used in this investigation was Type 124 P-1 cellulose film, manufactured by American Viscose Division, FMC Corporation. As received, this material contained 12.4% glycerol as a plasticizer, 6.7% water at 45% R.H., and a minute quantity of surface slip agent. Film thickness was 1.6 mils. For studies on unplasticized material, the glycerol was extracted by a water treatment. After drying, the thickness of the unplasticized films was about 1.4 mils. Aluminum electrodes were vapor deposited directly onto the specimens. A three-electrode arrangement was used for all measurements.

The film specimen is mounted between insulated brass electrodes in the sample chamber. The evacuated chamber can be immersed directly into

liquid nitrogen. Temperature control is achieved with a heater in thermal contact with the guarded electrode, and the temperature is monitored with a calibrated copper-Constantan thermocouple referenced to ice water. For all results reported, the heating rate was maintained at $0.82^\circ\text{K}/\text{min}$ and the chamber pressure was approximately 10^{-3} torr.

The depolarization current was measured with a Keithley 610 CR Electrometer. The usual precautions were taken for measuring small currents, to eliminate spurious rf pickup and leakage paths. The leakage resistance of the sample holder and vacuum feedthroughs was in excess of 10^{13} ohms.

Prior to data gathering, excess water was removed from the cellulose by conditioning the specimen, mounted in the sample holder, for a period of 10 hr or more at a chamber pressure of 10^{-3} torr. In most instances the specimen temperature was simultaneously elevated to 40°C . Higher conditioning temperatures were avoided because of possible structural damage. After treatment, water retention was estimated at less than 2%.⁸ It was not possible to determine the moisture content during the course of the experiment.

The temperature range of interest in this investigation was from -100° to $+50^\circ\text{C}$. Several preliminary measurements above 50°C , however, indicate the presence of one or more bands in the vicinity of 90°C . It is suspected that these may result from a space charge phenomenon, but this temperature region will require further investigation.

EXPERIMENTAL RESULTS

A summary of the polarization parameters and results for all data discussed in this report are included in Tables I and II. In Table I, the experiment number suffix G refers to cellulose plasticized with glycerol. E_p is the polarization field strength in kV/cm, T_p is the polarization temperature in $^\circ\text{K}$, and t_p is the total time during which the field was maintained, including the time of polarization at T_p , and the time during cooling to T_0 .

TABLE I
Experimental Parameters

Experiment no.	E_p , kV/cm	T_p , $^\circ\text{K}$	t_p , min	T_0 , $^\circ\text{K}$	T_{td} , $^\circ\text{K}$
6AG	74	296	57	185	185
5AG	74	211	22	177	177
7AG	74	273	53	232	217
4AG	74	244	65	185	185
9AG	37	279	15	263	263
8AG	37	273	48	230	223
10AG	18	273	60	233	222
11AG	112	273	60	232	213
12A	85	295	72	198	191
13A	85	273	72	188	188
14A	85	230	23	191	189
15A	85	283	16	263	250

TABLE II
Summary of Results^a

Experiment no.	Band I			Band II			Band III or IV			
	U_i eV	T_m °K	i_m^b amp	U_i eV	T_m °K	i_m^b amp	U_i eV	T_m °K	i_m^b amp	ω
6AG	0.27	(219)	(0.7)	*	272	10.0	*	*	*	
5AG	0.25	217	1.3	0.53	271	9.3	*	(298)	*	
7AG										0.44
4AG	0.25	218	(0.8)	*	270	4.9	0.61			0.47
9AG								289	(1.2)	
8AG				0.54	271	4.4	*	(300)	*	
10AG				0.51	270	2.2	*	(300)	*	
11AG				0.47	268	13.4	*	*	*	
12A	0.26	213	0.56				(0.55)	295	2.4	0.42
13A	0.29	215	0.57				*	294	1.3	0.37
14A	0.25	213	0.56							
15A							0.56	298	1.9	0.40

^a An asterisk (*) denotes that the band in question was observed, but that the value could not be estimated with any certainty.

^b Current $\times 10^{10}$.

At temperature T_0 , the external field was removed and the specimen open-circuited. T_{id} is the temperature at which the specimen capacitor was connected into the depolarization circuit.

In Table II the measured parameters U , T_m , and i_m , are included for each of the observed bands. U is the dipole activation energy in eV, T_m is the temperature at which the current maximum occurs in $^{\circ}\text{K}$, and i_m is the maximum depolarization current in amps ($\times 10^{10}$). A quantity in parenthesis denotes that the value is at best an estimate, usually because of the proximity of another band. An asterisk denotes that the band in question was observed, but that the value could not be estimated with any certainty. The parameter ω is Chen's criterion⁹ for distinguishing between first- and second-order kinetics, and is a measure of the asymmetry of the band. Experimentally, $\omega = (T_u - T_m)/(T_u - T_l)$, where T_u and T_l are the temperatures at which the current is one half its maximum value. For a monomolecular process such as the depolarization phenomena, the theoretical value is 0.43, whereas for second-order kinetics the value is around 0.52.

Plasticized Cellulose

A typical depolarization current spectrum for cellulose films plasticized with glycerol is shown in Figure 1 (experiment 6AG). The spectrum is

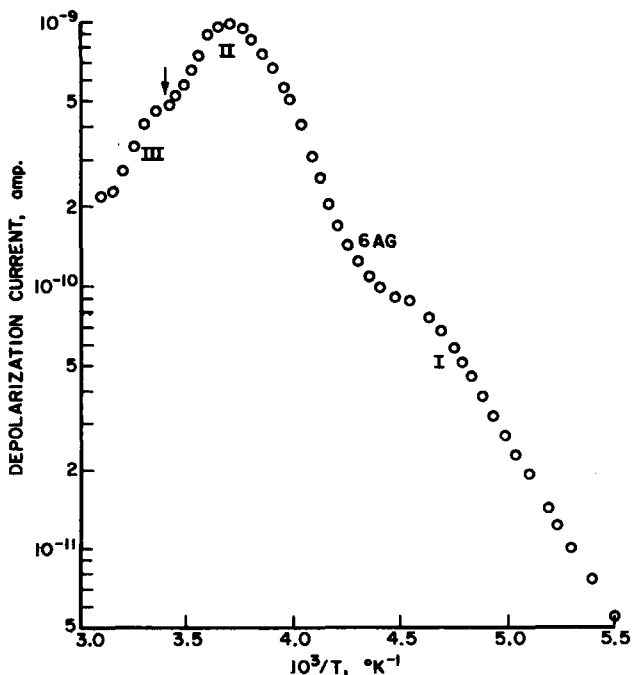


Fig. 1. Depolarization current spectrum for plasticized cellulose. The arrow defines the polarization temperature. All polarization parameters are included in Table I.

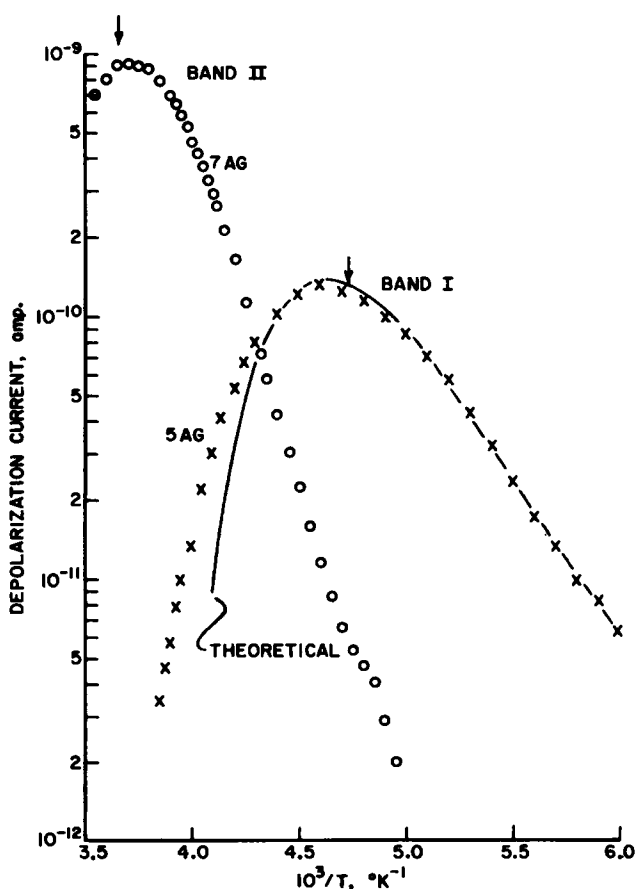


Fig. 2. Thermal depolarization current results for bands I and II. The separation technique and the theoretical curve are discussed in the text.

composed of at least three bands, labelled I, II, and III, in the direction of increasing temperature. Bands I and III appear only as shoulders on opposite sides of the intense central band II. The arrow on Figure 1, and on all subsequent figures, defines the polarization temperature T_p .

It was possible to separate the weaker band I from II by originally polarizing the specimen at lower temperatures. This is shown on Figure 2 as curve 5AG. The current maximum occurs at 217°K ($10^3/T = 4.6$), and the dipole activation energy, U , as determined from the low-temperature side of the maximum, is computed as 0.26 eV or 6 kcal/mole. Using these values, it is possible to generate a theoretical curve for the depolarization current band (eq. (1), reference 2; see also reference 10). This is shown on Figure 2 where theory and experiment have been fitted at the maximum.

The difference between the magnitudes of the isolated band I and the shoulder depicted on Figure 1 results from a partial discharge of the band in the latter case. This occurs because the specimen was not cooled to a

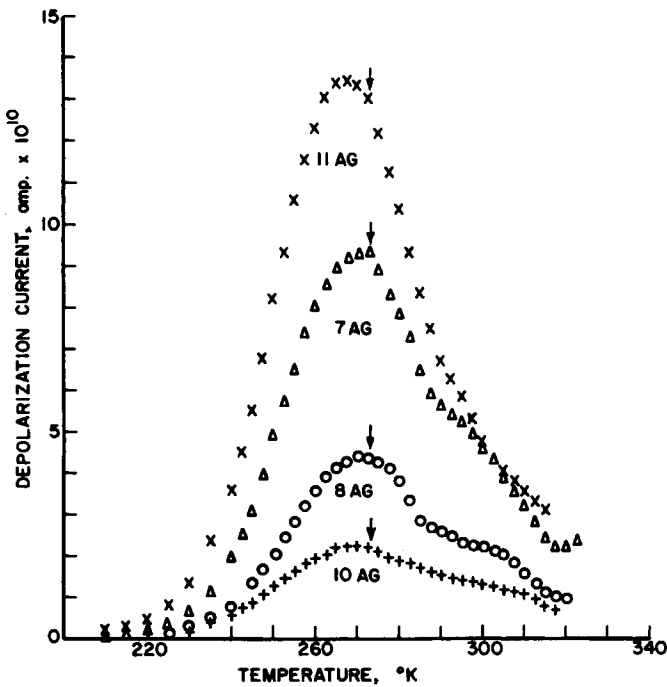


Fig. 3. Depolarization current spectra depicting bands II and III at various polarization field strengths.

sufficiently low temperature, beyond the tail of band I. A partial discharge should not affect the computed activation energies or T_m , but will affect any calculations involving the band area. A separate measurement initiated at very low temperatures (150°K) reveals that 5AG represents the true band area.

The low temperature behavior of band II was determined by allowing band I to completely discharge, and is shown as curve 7AG on Figure 2. The measured parameters for this band are $T_m = 271^\circ\text{K}$ and $U = 0.51\text{ eV}$. Because of the prominence of band II, it was not possible to completely isolate band III. In one measurement band II was allowed to discharge before heating commenced (experiment 9AG in Tables I and II), but the results are still believed to be affected by a remnant of band II on the low-temperature side of III. Band III could be eliminated by polarizing at lower temperatures (experiment 4AG).

The possibility that the observed bands were due to a space charge phenomena was examined by performing a series of measurements at different polarization field strengths, while keeping other parameters constant. These results are shown in Figure 3, where, in the order of increasing magnitudes, the field strengths were 18, 37, 74, and 112 kV/cm, respectively. (These curves additionally reveal the presence of band III in the vicinity of 300°K .) A plot of the depolarization band area versus polarization field strength is linear, suggesting that space charges are not responsible

for the occurrence of these bands.² Further evidence that these bands are dipolar in origin is deduced by noting that no relationship exists between the temperature of the maximum, T_m , and the polarization temperature, T_p . This can be seen by comparing the values of T_m and T_p in Tables I and II. The observed values of T_m for each band are (nearly) constant for all measurements and independent of T_p . The generally fair agreement between the experimental values of ω (Table II) and the theoretical value (0.43) is also suggestive of a dipolar origin for these bands. Utilization of this criterion, however, requires completely isolated bands. If a remnant band is present on either side of the main band, it can cause ω to be greater or less than the theoretical value, depending on which side of the main band the remnant falls.

The activation energies for the data shown in Figure 3, computed from a plot of \ln current versus inverse temperature, are independent of E_p . A dependence of U upon E_p has been reported for a band in the depolarization spectrum of poly(ethylene terephthalate).⁴ The variation in the computed activation energies (Table II) probably arises because of remnants of band I still present on the low temperature side of band II.

Unplasticized Cellulose

The depolarization current spectrum for a typical experiment on unplasticized cellulose is depicted in Figure 4 as curve 12A. The most noticeable distinction between these results and those discussed in the preceding section is the absence of band II at 271°K. The low-temperature band, 14A, was isolated by polarizing at lower temperatures. For this latter band, $U = 0.26$ eV and $T_m = 214^\circ\text{K}$. These values are essentially identical with those reported for band I in the plasticized cellulose, implying that these are the same bands. This new band is accordingly labeled as band I. The displacement of the current maximum from 217° to 214°K, upon removal of the plasticizer, however, is unexpected. The effect of a plasticizer would be to lower the temperature at which the maximum occurs. This small temperature shift of three degrees is probably due to experimental error.

The isolated high-temperature band, 15A, shown on Figure 4 has parameters $U = 0.56$ eV and $T_m = 298^\circ\text{K}$. This band is labeled band IV. From a number of independent measurements, the values of T_m for band IV varied from 294° to 309°K. This variation in T_m was independent of T_p , but was inconsistent with results for the other bands, all of which yielded reproducible results. It is believed that this variation is due to a slightly changing moisture content in the specimens. As noted earlier, there is no provision for determining the moisture content during the experiments. Several measurements on samples which had not experienced the conditioning period yielded $T_m = 286^\circ$ and 290°K for this band, with current magnitudes comparable to those reported for the conditioned specimens. Together, these results suggest that band IV arises in the

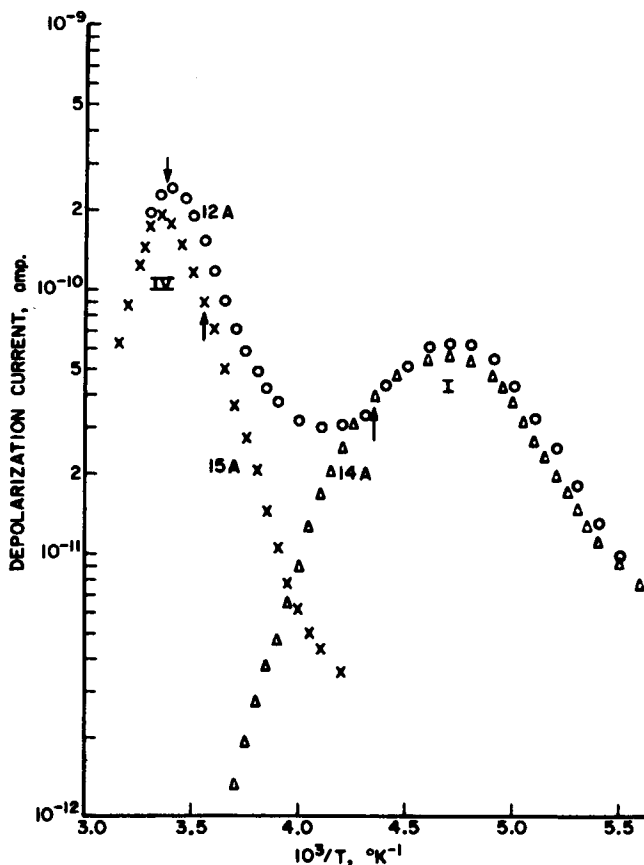


Fig. 4. Typical depolarization results for an unplasticized cellulose film.

amorphous regions where water is acting as a plasticizer, but that the water itself is not responsible for the observed band.

It seems probable that band IV would also shift to lower temperatures when glycerol was present as a plasticizer, and perhaps be obscured or contribute to band II. This reasoning suggests that band IV differs from band III found in the plasticized cellulose.

DISCUSSION AND CONCLUSIONS

Band II

The absence of band II in the results for the unplasticized cellulose implies that this band originates with the glycerol plasticizer. This is perhaps more evident in a plot of depolarization current versus temperature as shown in Figure 5. From previous arguments it has been concluded that band II is a true orientation band, with average parameters $U = 0.51$ eV and $T_m = 271^\circ\text{K}$. Using these values, an attempt was made to

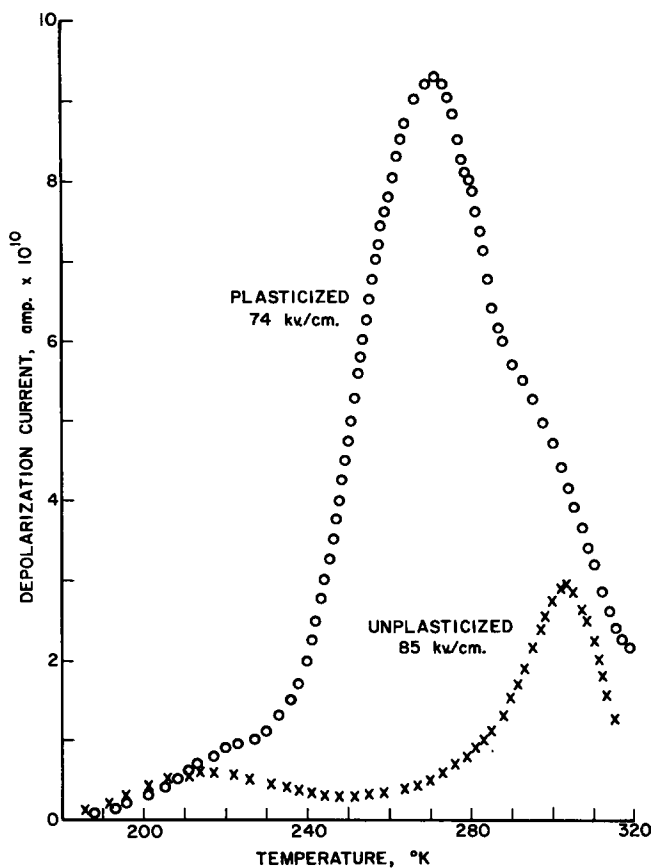


Fig. 5. Comparison of results for glycerol plasticized and unplasticized cellulose films.

fit experiment with the theoretical expression for the single relaxation process (eq. (1), reference 2). This attempt was unsuccessful. Aside from the difficulties in isolating band III, it appears that the differences between theory and experiment can only be explained by assuming at least two subbands combining to produce band II. This assumption is not pure conjecture, for a close examination of Figures 3 and 5 reveals what appears to be an additional shoulder at 280°K on the high-temperature side of band II. A successful synthesization of all the experimental results shown in Figure 3 was accomplished by assuming two subbands. There is, of course, no absolute justification for such a model at present.

For the preliminary results reported here, the emphasis has been on obtaining typical depolarization current spectra for cellulose. This will provide a basis for future work in which certain modifications are made, e.g., substitutions. The observance of a band associated with the glycerol, however, suggests that this technique may also assist in elucidating the mode of action of plasticizers in cellulose. The effects of changing glycerol

contents, for example, should be manifest in the depolarization current spectrum.

Band IV

A second-order transition is known to exist in dry cellulose in the vicinity of 25°C (298°K)¹¹⁻¹⁴ and is apparently related to the amorphous structure. At temperatures above the transition temperature, the increasing accessibility to water adsorption is interpreted as hydrogen bond breakage in the dry material, allowing greater lability for some of the hydroxyl groups. According to Wahba,¹⁴ one class of hydrogen bonds break at a greater proportion below the transition at 298°K than above it.

It seems reasonable to consider the existence of band IV as being associated with this second-order transition. Both phenomena are assumed to arise within the amorphous regions, and the average value of T_m in the "dry" unplasticized material is near 298°K. If the description of the second-order transition is accurate, then the depolarization current method should be suited for investigation of this phenomenon, since this technique is sensitive to the density of polar groups and the ease with which they can respond to the external electric field. It would seem probable that in the presence of a strong electric field, which causes changes in the orientation of the dipoles, normal reformation of the hydrogen bonds with decreasing temperature would be hindered or prevented. These labile hydroxyl groups could then give rise to the observed depolarization band upon warming of the specimen.

Although such preliminary considerations demonstrate the reasonableness of associating band IV with the second-order transition in cellulose, definite conclusions will require further investigation. In particular, the use of different field strengths, and values of T_p above and below the transition temperature, could help to clarify the nature of this phenomenon. In closing, it is perhaps worthy of note that the depolarization band observed in the vicinity of 90°C, mentioned earlier, coincides with the temperature of the next transition reported for cellulose.¹⁵

Band I

Band I occurs in both the plasticized and unplasticized cellulose, with average parameters $U = 0.26$ eV and $T_m = 215^\circ\text{K}$. The lack of sensitivity to the presence of the plasticizer suggests that this band originates in the crystalline regions.

It is tempting to compare this band with the known low-temperature band which occurs in the ac dielectric loss spectrum of cellulose. For example, in dry cellulose at 10 kHz, Seidman and Mason¹⁶ observed a maximum in the dielectric loss near 223°K. They attributed this loss peak to hydroxyl group rotations and computed the free energy of activation and the enthalpy as 7.7 and 8.8 kcal/mole, respectively. With increasing moisture levels, the maximum shifted to lower temperatures, indicating a plasticizing action for the water. Mikhailov et al.¹⁷ have also used ac

techniques (at 1000 Hz) to investigate this temperature range in regenerated cellulose films. They observed a loss maximum near 206°K for cellulose, but when other groups were substituted for the hydroxyl group on C6, the loss maximum disappeared. It was thus concluded that the observed band was due to the lability of the primary —OH group and the —CH₂ group which joins it to C5 of the pyranose ring.

Certain similarities are in evidence between this dielectric loss maximum and band I. First, the band I activation energy of 0.26 eV or 6 kcal/mole agrees favorably with those results of Seidman and Mason, and the temperatures of the maxima are comparable for both. Second, the density of polar groups responsible for band I may be estimated, and this value is comparable to the concentration of —CH₂OH groups in the material. The density of polar groups, N_p , is estimated from the band area (eq. (4), reference 2). From the area of curve 5AG, using the dipole moment for a hydroxyl group as 1.7 Debyes, N_p is estimated as 8×10^{21} cm⁻³. The density of —CH₂OH groups in the cellulose is approximately 5×10^{21} cm⁻³. This order of magnitude agreement supports the suggestion that band I may originate with primary hydroxyl group orientations.

There are also several differences, however. Band I is apparently insensitive to plasticizers (at least glycerol), whereas the dielectric loss maximum shifted with changing moisture contents. Furthermore, discrepancies exist between the relaxation times computed for the two phenomena. A definitive experiment will be to substitute other groups for the primary hydroxyl group. In xylan, for example, no depolarization current band would be expected at 215°K if the supposition of C6 hydroxyl group orientations is correct.

SUMMARY OF CONCLUSIONS

1. The low-temperature depolarization current bands observed in plasticized and unplasticized cellulose appear to be dipolar in origin, suggesting that this technique can be useful for investigating the effects of thermal, mechanical, or chemical treatments which can alter the density, type, or local environment of the polar groups.
2. A low-temperature band occurs in both plasticized and unplasticized cellulose at the same temperature and with the same activation energy (band I). This band is tentatively believed to be associated with primary hydroxyl group orientations.
3. Depolarization bands are observed in both plasticized and unplasticized cellulose in the vicinity of 298°K. It is suggested that the band in the unplasticized material (band IV) may be related to the second-order transition in cellulose at 25°C. The band in the plasticized cellulose has not been examined in detail.
4. An intense band at 271°K occurs only in the plasticized cellulose, and thus apparently originates with the glycerol plasticizer. This band is believed to be the combination of two less intense bands, both presumably related to the glycerol or its associated water.

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