Thermally stimulated depolarization effect in thiourea–formaldehyde condensate

Hari Singh Nalwa and Padma Vasudevan
Department of Chemistry and Centre for Rural Development and Appropriate Technology, Indian Institute of Technology, New Delhi 110016, *India*

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A thiourea–formaldehyde condensate was synthesized in an acid medium and characterized by elemental analysis, infra-red spectroscopy, and thermal methods of analysis. The thermally stimulated depolarization effect was studied in samples polarized under different conditions. The results indicate two distinct transitions in the temperature ranges 94°–100°C and 122–126°C. The polarization–depolarization phenomena were correlated with the physicochemical changes occurring in the matrix. Depolarization kinetics data such as activation energy and relaxation times of the electrets are reported.

Keywords Thermally stimulated depolarization effect; thiourea–formaldehyde condensate; transitions; physicochemical changes; activation energy; relaxation time

INTRODUCTION

When an electret is heated, depolarization occurs leading to evolution of current, termed thermally stimulated current (t.s.c.). This technique has become one of the basic tools for the identification and evaluation of dipole reorientation processes, trapping and recombination levels of dielectric materials[1,2]. In our laboratories, the thermally stimulated depolarization (t.s.d.) effect has been studied in thermosetting materials such as epoxy[3] and phenolic[4] resins. The results indicate that t.s.d. is an important electro-analytical technique[5] in elucidating the mechanisms of curing during condensation of linear and low molecular weight polymers present in the partially cured state. It was considered of interest to extend this type of work to thiourea–formaldehyde (TUF) condensate, which is also a thermosetting material. Preliminary results on the electrical properties of this condensate have already been discussed[6]. The present paper further analyses the nature of t.s.d. characteristics.

EXPERIMENTAL

The TUF condensates was synthesized by reacting thiourea with formaldehyde in acetic acid: 1 mol of thiourea and 1 mol of 37% formaldehyde was condensed in 500 ml of 50% acetic acid at room temperature. A white material was precipitated. It was filtered off and washed several times with distilled water. The resulting mixture of condensates was dried at room temperature and was labelled as TUFA. TUFA condensate (10 g) was dissolved in 50 ml of dimethylformamide for fractionation. It was precipitated with distilled water and two fractions were obtained ($TUFA_1$ and $TUFA_2$). Only the second fraction $TUFA_2$ was used in the present study. The material obtained was characterized by elemental analysis, i.r. spectroscopy and thermal methods of analysis.

The i.r. spectra of $TUFA_2$ samples were recorded using the KBr pellet method over the range 400–4000 cm^{-1}. Some samples of $TUFA_2$ were also heated at 95°, 126° and 150°C for 1 h, cooled and their i.r. spectra were examined to study the chemical changes during heating.

For some $TUFA_2$ samples, the gaseous products of thermal decomposition were recorded by the gas chromatographic technique. $TUFA_2$ samples were heated at 94°, 124°, 140° and 190°C and their gas chromatograms were taken.

The weight loss occurring during heating the samples was recorded by t.g.a. and to examine the thermal transitions the d.s.c. technique was employed.

The depolarization characteristics of TUF samples were studied as follows: samples with a polarization field E_p were heated up to the polarization temperature T_p, and the temperature was held constant for a time t_p; after cooling to room temperature, the voltage source was disconnected and the t.s.d. was recorded at a uniform heating rate. Polarization conditions employed for $TUFA_2$ condensate were: $E_p = 4, 7$ and 10×10^3 V cm^{-1}, $T_p = 60°$, 75° and 90°C and $t_p = 120$ min. Depolarization spectra were recorded at heating rates of 2, 4, 6, 8 and 10°C min^{-1} using different electrode materials such as aluminium, silver, copper and stainless steel.

RESULTS AND DISCUSSION

Characterization

The elemental analysis for the samples of $TUFA_2$ condensates show reproducibility of ±0.5% with average values C = 26.17%, H = 4.95%, N = 29.64%, S = 35.15% and O = 4.09%, and the compound analysed has an empirical formula $C_8H_{18}N_8S_4O$. This matches with the elemental composition and structural formula suggested by Staudinger and Wagner[7], who also reported similar preparation of TUF condensates in an acid medium using acetic or hydrochloric acids. The molecular weight of the compound determined by the depression in freezing point

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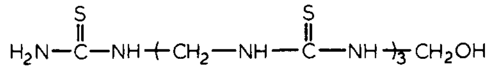
Table 1 I.r. spectral data of TUFA$_2$ condensates

I.r. absorption bands reported[8] in methylene bis-thiourea (I) and dimethylene trithiourea (II)			I.r. absorption bands reported[8] for monomethylol thiourea		I.r. absorption bands observed in the present TUFA$_2$ sample	
I.r. bands (cm^{-1})		Assignment				
I	II		I.r. bands (cm^{-1})	Assignment	I.r. bands (cm^{-1})	Assignment
679	675	–	695	SCN$_2$	680	SCN
710	708	SCN$_2$	706	SCN$_2$	710	SCN
944	945	N–CH$_2$–N	955	–N–CH$_2$–O	950	–N–CH$_2$–N and –N–CH$_2$–O
999	–	–	1012	CH$_2$	1010	–CH$_2$OH and –CH$_2$
1080	1088	–NH$_2$	1095	NH$_2$	–	–
1133	1140	–N–CH$_2$–N	1130	N–CH$_2$O	1140	–N–CH$_2$–N
–	–	–	1230	OH	–	–
1273	1274	–CH$_2$ and –NH	–	–	1275	–CH$_2$ and –NH
1304	–	–	–	–	–	–
1325	–	–	–	–	–	–
1340	1342	–NH	1351	NH	1340	–NH
1362	1360	–SCN$_2$	1370	SCN$_2$	–	–
1407	1393	–CH$_2$	1400	CH$_2$	–	–
1440	1447	–CH$_2$	–	–	1450	CH$_2$
1460	–	–CH$_2$	1468	CH$_2$	–	–
1527	1525	–CN$_2$	1525	CN$_2$	1520	CN$_2$
1547	1545	–CN$_2$	1551	CN$_2$	–	–
–	–	–	1562	–	–	–
1611	1608	–NH$_2$	–	–	–	–
1620	1616	–NH$_2$	1622	NH$_2$	1620	NH$_2$
–	–	–	–	–	1660	–
–	–	–	2900	CH$_2$	2800	CH$_2$
–	–	–	3240	NH$_2$ and NH	–	–
–	–	–	3400	NH$_2$ and OH	3330	NH$_2$ and OH

of caprolactam was 370. The condensate melts at 213°–215°C. Much information on the chemical structure of the TUF condensate can be obtained from the i.r. spectral studies. *Table 1* lists the main i.r. absorption bands for TUFA$_2$ samples together with the assignments. The general features of the i.r. spectra, elemental analysis and molecular weight seem to confirm the proposed chemical structure of TUFA$_2$ as monomethylol trimethylene tetrakisthiourea:



$$H_2N-\overset{\overset{\displaystyle S}{\|}}{C}-NH\left[CH_2-NH-\overset{\overset{\displaystyle S}{\|}}{C}-NH\right]_3CH_2OH$$

In this condensate, thiourea segments are linked through methylene bridges.

Thermally stimulated depolarization characteristics

Figure 1 shows the effect of T_p on the electret. As T_p increases, the t.s.d. peak shifts to higher temperatures. *Figure 2* represents the effect of E_p on the t.s.d. peak positions, which shift to higher temperatures with increasing electric field strength. *Figure 3* shows the effect of electrode materials on the t.s.d. curves of the samples. In the case of an aluminium electrode, the t.s.d. peak was observed at 122°–126°C; for copper, peaks at 122° and 146°C; for silver, peak at 130° – 134°C; and for stainless steel, peak at 138°C. In *Figure 4*, the effect of heating rates on t.s.d. peaks is depicted. An additional t.s.d. peak at 94°C was recorded at a heating rate of 2°C min^{-1}.

Activation energies E_a have been calculated from the semilogarithmic plots of currents (i) in the initial rise of the depolarization peak[9] versus $1/T$ (*Figure 5*), and by Bucci–Fieschi[10] plots (*Figure 6*). The E_a values were also

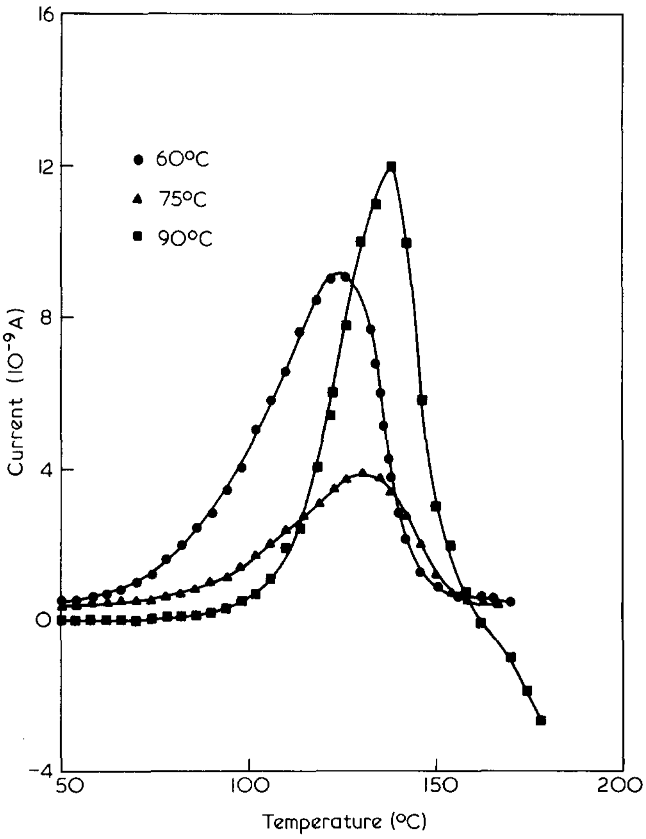


Figure 1 Effect of polarization temperature on t.s.d. current spectra of samples polarized at E_p = 4 x 10^3 V cm^{-1}, t_p = 2 h, T_p = 60°, 75° and 90°C and β = 4°C min^{-1}

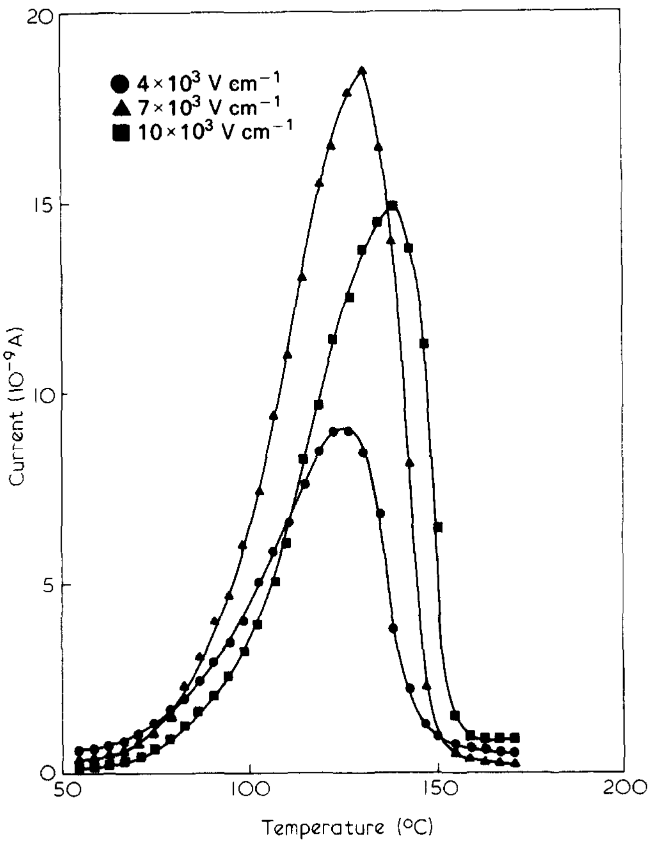


Figure 2 Effect of polarization field on t.s.d. current spectra of samples polarized at T_p = 60°C, t_p = 2 h, E_p = 4 x 10^3, 7 x 10^3 and 10 x 10^3 V cm^{-1} and β = 4°C min^{-1}

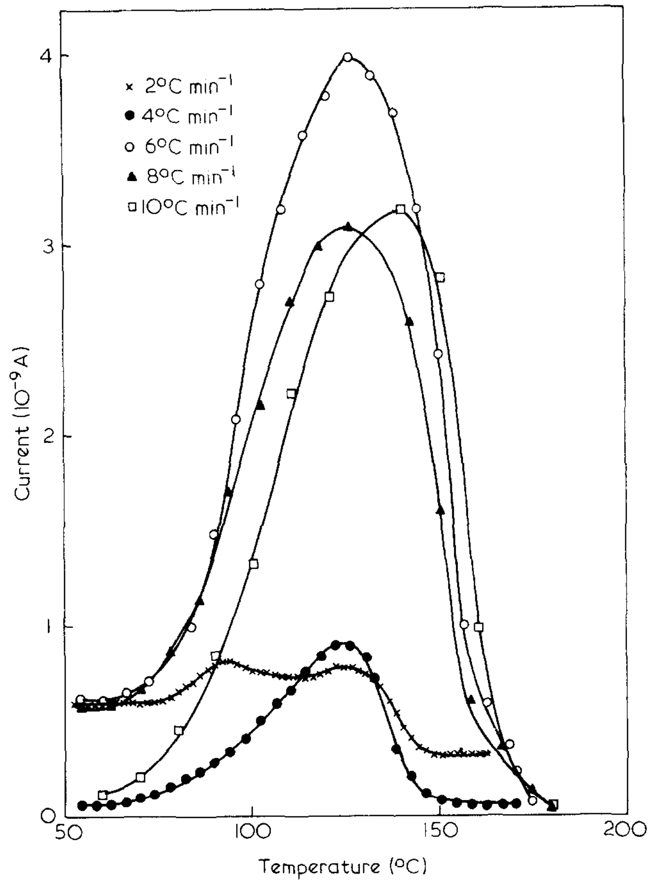


Figure 4 Effect of heating rate on t.s.d. current spectra of samples polarized at T_p = 60°C, E_p = 4 x 10^3 V cm^{-1}, t_p = 2 h and β = 2, 4, 6, 8 and 10°C min^{-1}

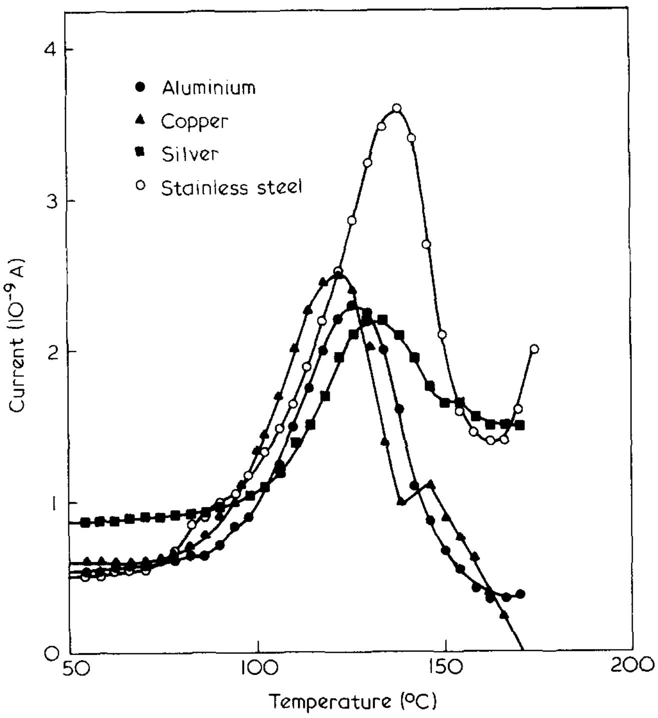


Figure 3 Effect of electrode material on t.s.d. current spectra of samples polarized at T_p = 60°C, E_p = 4 x 10^3 V cm^{-1}, T_p = 2 h and β = 4°C min^{-1}. Electrode materials used were aluminium, copper, silver and stainless steel

determined by the method of Grossweiner[11]. *Table 2* lists the E_a values calculated from these methods. The corresponding values of relaxation times were calculated using Arrhenius equations[12] from E_a values obtained in the initial rise method (*Table 3*).

It is well known that, in homogeneous systems, polarization and depolarization phenomena are associated with dipolar and space-charge effects[13], while the Maxwell–Wagner effect[14] (interfacial polarization) becomes operative in a heterogeneous system. For example, the presence of an air gap creates heterogeneity giving rise to t.s.d. peaks. In the present study, the t.s.d. peaks were obtained from samples coated with aluminium as well as sandwiching them between aluminium electrodes. In both the cases, similar t.s.d. spectra were observed, indicating that in the sandwiched system also there is no air gap. Thus interfacial polarization due to an air gap is not operative. Since the charging voltages are low (10^3 V cm^{-1}), the homocharges by injection may not be

Table 2 Activation energies of TUFA$_2$ electret calculated from different methods

T_{max} (°C)	Initial-rise method[9] (eV)	Bucci–Fieschi method[10] (eV)	Grossweiner method[11] (eV)
122	0.50	0.52	0.65
130	0.72	0.73	0.87
138	1.15	1.13	1.32

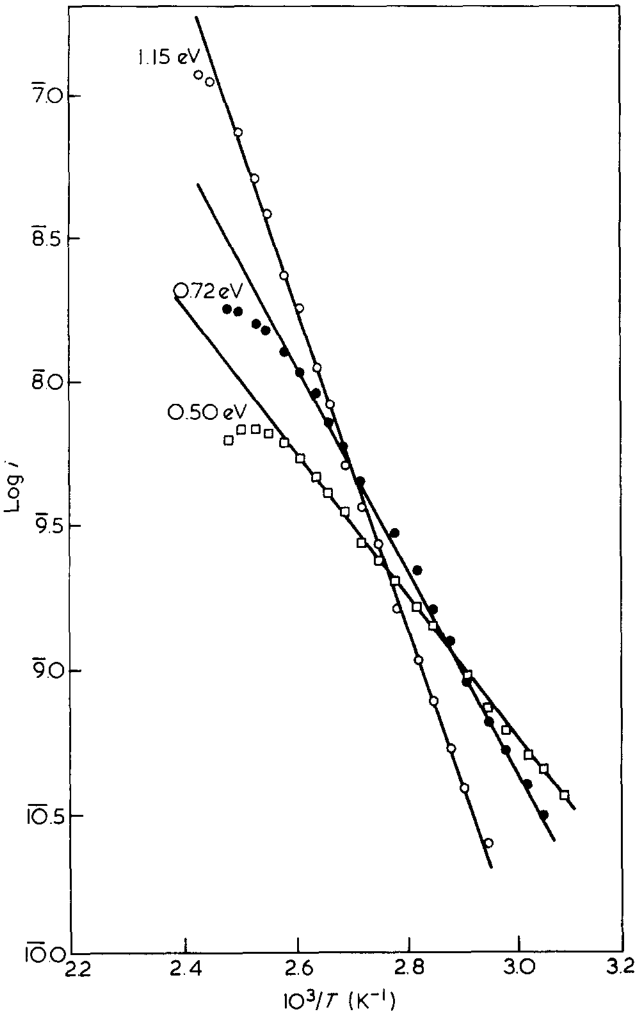


Figure 5 Log current (*i*) versus 1/*T* for determination of activation energy (E_a) by initial-rise method for the t.s.d. peaks: 122°, 130° and 138°C

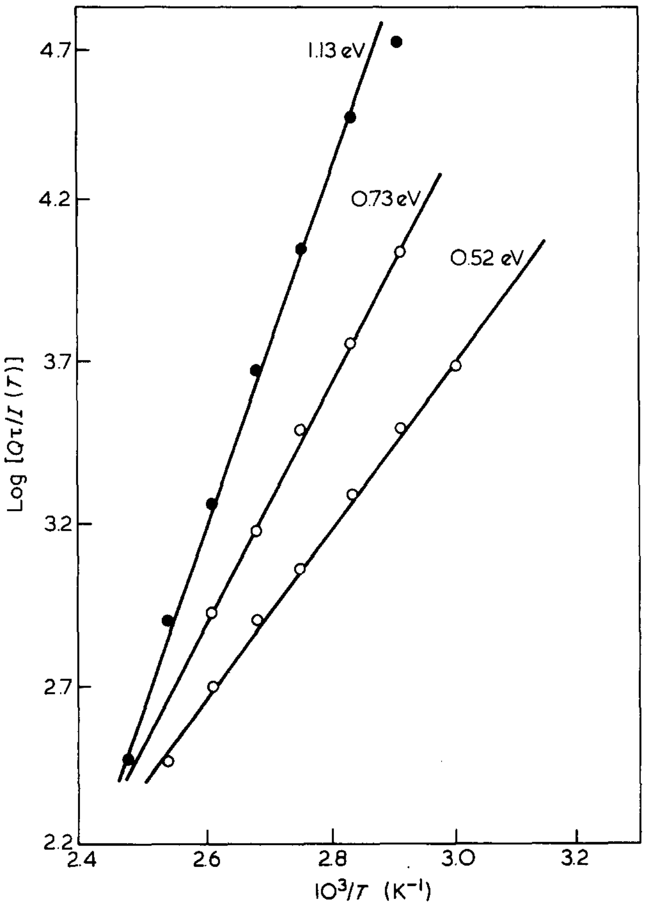


Figure 6 Determination of activation energy (E_a) from Bucci–Fieschi plots for the t.s.d. peaks: 122°, 130° and 138°C

present. Hence only polarization by dipole orientation and space-charge effect are considered. The expected variations in t.s.d. peak with poling conditions for these two types of mechanisms have been summarized by Van Turnhout and others[14].

It has been shown that t.s.d. arising from dipole orientation polarization depends linearly on E_p and the maximum current (I_{max}) shows linear E_p dependence[15]. For space-charge polarization a field effect is also known[16], I_{max} varying non-linearly with E_p. Reichle *et al.*[17] have shown that a space-charge peak depends on electrode materials. In the present case, as seen from the *Figures 2* and *3*, the T_{max} shifts to higher temperature with T_p and E_p. The t.s.d. peak at T_p of 60°C, which is not fully developed, shifts to the higher value of 130°C for T_p of 75°C, and 138°C at $T_p = 90$°C. The t.s.d. peak for $T_p = 90$°C is sharp and fully developed. On increasing E_p, keeping T_p at 60°C, the peak shifts to higher T_{max}. The t.s.d. peak position is also affected by electrode material, as seen from *Figure 3*. When the rate of heating is reduced from 4°C min^{-1} to 2°C min^{-1}, there is a split into two t.s.d. peaks at 94°C and 122°C, indicating the possibility of more than one mode of polarization. Thus, though the data taken together cannot conclusively establish the mechanisms of depolarization, the trends are indicative of space-charge polarization. Besides physical effects, Stupp

Table 3 Depolarization kinetics data obtained for TUFA$_2$ electret

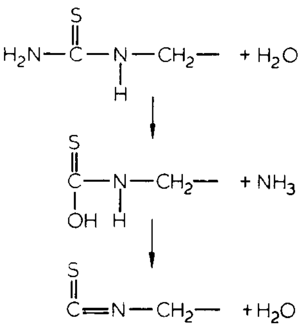
T_{max} (°C)	E_a (eV)	τ_0 (s)	τ_{300} (s)	τ_{300} (day)	τT_{max} (s)	τT_{max} (day)
122	0.50	1.69×10^{-4}	4.25×10^4	0.49	4.05×10^2	0.00468
130	0.72	2.90×10^{-7}	3.62×10^5	4.18	2.93×10^2	0.00339
138	1.15	1.5×10^{-12}	3.17×10^7	366.8	1.91×10^2	0.00221

T_{max} is the temperature of the t.s.d. peak
τ_0 is the inverse of the attempt to escape frequency
τ_{300} is the relaxation time at 27°C
τT_{max} is the relaxation time at T_{max}

and Carr[18] have shown that chemical changes can be associated with the t.s.d. peaks. In the present sample, heating will lead to further condensations, which would also affect the t.s.d.

Physicochemical changes occurring in the condensate during thermal treatment

To study the changes that occur during heating, the variations in the i.r. spectra of the samples at different temperatures were studied. *Table 4* lists the i.r. spectra after heat treatment, i.e. after heating at (a) 95°C, (b) 126°C and (c) 150°C. For recording the effect of temperature on i.r. absorption bands, all the samples were kept at these temperatures for 1 h. The i.r. bands appearing and disappearing after thermal treatment have been listed in *Table 4*. It is seen that the intensity of the bands at 680 and 710 cm^{-1} decreases on heating. These bands are assigned to –SCN vibrations, which shows that the structure –N–C–N is being disturbed. Also on heating up to 126°C, the intensity of the bands at 950 and 1010 cm^{-1} seems to decrease, and they tend to disappear on heating to higher temperatures around 150°C. Since the band at 950 cm^{-1} is attributed to $-N-CH_2-N$ or $-N-CH_2-O$ and the band at 1010 cm^{-1} being for $-CH_2OH$ and $-CH_2$, this is possibly indicative of increased crosslinks with breakdown at higher temperatures. A similar behaviour is noted for a band at 1140 cm^{-1} which is attributed to $-N-CH_2-N$ vibration. Also the band at 1450 cm^{-1}, possibly due to $-CH_2$, disappears above 150°C. Finally, the most interesting feature is the appearance of a band at 2060 cm^{-1} on heating the sample at 150°C. These spectral changes may be interpreted by curing effects with loss of water at higher temperature. We proposed that the water produced during curing may hydrolyse the thiourea end group. This scheme explains the disruption of the $-CN_2$ unit to form the $S=C=N-$. This would explain the appearance of the 2060 cm^{-1} band, which is normally attributed to an isothiocyanate linkage. It is well known that ammonium cyanate can form urea on heating. If such a process is reversible, thiourea moiety on heating forms isothiocyanate. At intermediate levels of heating, say up to 126°C, it is possible that crosslinking occurs between $-CH_2OH$ and $-NH_2$ groupings to form methylene bridges as stated above.



In order to identify the gaseous products emitted during heating, a gas chromatogram of the sample was taken at different temperatures as shown in *Figure 7*. At 94°C, only the evolution of water was observed; when the sample was heated at 124°C, two peaks were identified corresponding to water and ammonia. At 150°C these two gaseous products were also liberated, but the intensity was less compared to that at 124°C. The polymer matrix decomposes extensively beyond 190°C.

The t.g.a. and d.t.g. plots are shown in *Figure 8*. In the temperature range 100°–150°C, only 3–5% weight loss is indicated. Since the molecular weight of the compound is 370, the loss of either water or ammonia does not correspond to more than 5% of the matrix. However, further heating up to 200°C results in more than 75% loss, owing to the total decomposition of the matrix. The technique of d.s.c. was also applied to identify the thermal transition in the polymer matrix. The d.s.c. scan of the uncured sample at a scanning rate of 4°C min^{-1} is shown in *Figure 8*. A sharp endothermic peak was observed around 126°C. This is probably a softening point where physical mobility is available to the molecular segments and side groups. It may be noted that t.s.d. peaks were also observed near this temperature. Possibly the higher mobility in the matrix helps in depolarization in a cooperative way. This also simultaneously enhances chemical condensation reactions since with increased

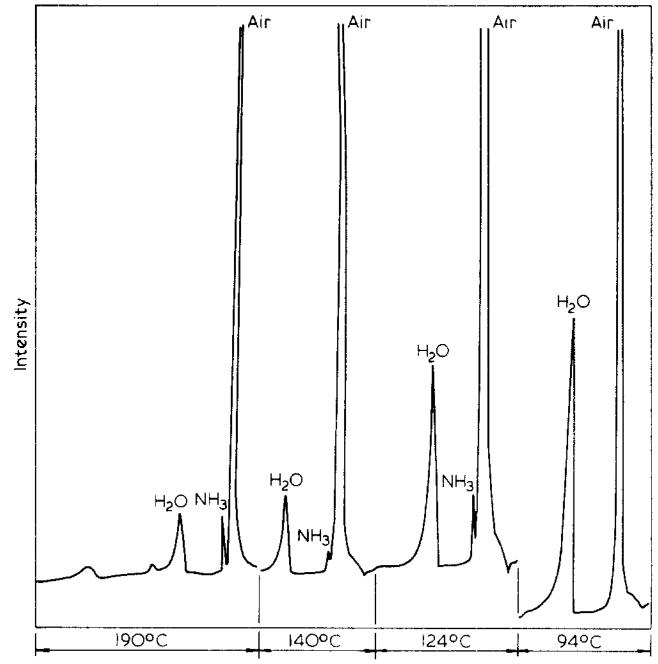


Figure 7 Gas chromatogram spectra of samples at 94°, 124°, 140° and 190°C

Table 4 I.r. spectral data of $TUFA_2$ condensate after heating at different temperatures

Temperature (°C)	I.r. absorption band observed (cm^{-1})												
	680	710	950	1010	1140	1275	1340	1450	1520	1620	1660	2060	3330
Room temp.	s	s	vs	s	s	w	w	s	vs	vs	s	a	vs
95	s	w	s	s	s	s	s	vs	w	wp	wp	a	vs
126	s	wp	w	w	vw	s	s	s	vs	vw	a	a	vs
150	wp	vw	wp	wp	vw	w	w	s	vs	w	a	d	vs

s = strong, w = weak, p = present, a = absent, d = develops, vw = very weak, vs = very strong, wp = weak present

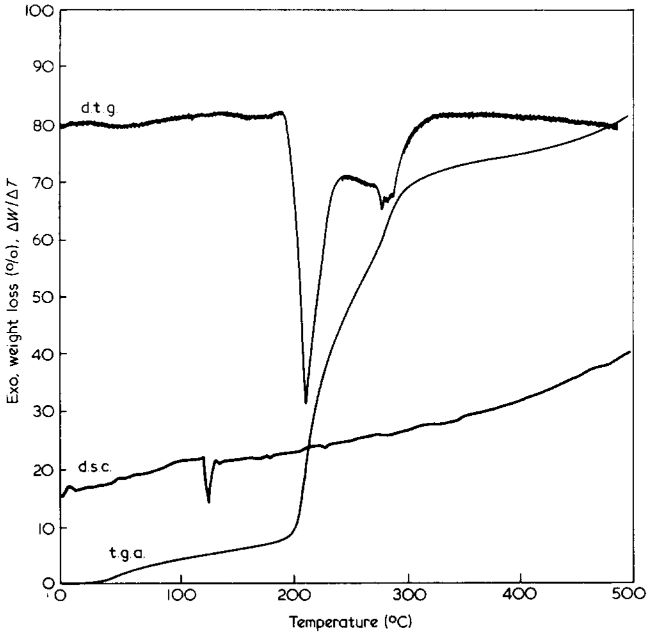


Figure 8 D.t.g., t.g.a. and d.s.c. scans of $TUFA_2$ samples

mobility the reacting groups can get oriented in conformations conductive to the chemical interaction.

CONCLUSIONS

Thus, the electrical measurements along with the variations in i.r. spectral data and results of thermal methods of analysis indicate the presence of two distinct transition regions in the temperature ranges 94°–100°C and 122°–126°C. These peak positions were reproducible on using different sets of fresh samples. It is proposed that up to 94°–100°C, trapped water as well as water formed *in situ* by further condensation is present in the matrix. This is reflected in a decrease in resistivity[6]. On further heating, the trapped water is slowly lost and correspondingly the electrical resistance increases[6]. However, as heating is continued, chain mobility is increased, and at around 122°–130°C the water produced by condensation *in situ*, instead of evaporating, hydrolyses the thiourea end groups, with the formation of –SCN– groups. Also the methylol group may be losing water to form methyleneimide linkage (–CH=N). Thus it is proposed that the t.s.d. peaks at ~94°–100°C are due to a physical effect associated with trapped water, and the one at ~122°C is attributed to both physical and chemical transitions. Studying thermally stimulated currents in such matrices and comparing the results with i.r. and thermo-analytical data helps to locate the temperature regions at which intensive curing occurs through condensation. Thus t.s.d. studies form a useful electro-analytical technique in examining the curing process.

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REFERENCES

1 Van Turnhout, J. 'Thermally Stimulated Discharge of Polymer Electrets', Elsevier, 1975
2 Pillai, P. K. C., Nair, P. K. and Nath, R. *Polymer* 1976, **17**, 921
3 Pillai, P. K. C. and Goel, M. *J. Electrochem. Soc.* 1973, **120**, 395
4 Viswanathan, P. S. and Vasudevan, P. *Angew. Makromol. Chem.* 1982, **102**, 17
5 Viswanathan, P. S., Ph.D. Thesis, Delhi, 1980
6 Nalwa, H. S. and Vasudevan, P. *Eur. Polym. J.* 1981, **17**, 145
7 Staudinger, H. and Wagner, K. *Makromol. Chem.* 1954, **12**, 168
8 Becher, H. J. and Griffel, F. *Chem. Ber.* 1958, **91**, 691, 2025
9 Garlick, G. F. J. and Gibson, A. F. *Proc. Phys. Soc.* 1948, **61**, 574
10 Bucci, C. and Fieschi, R. *Phys. Rev. Lett.* 1964, **12**, 16
11 Grossweiner, L. I. *J. Appl. Phys.* 1953, **24**, 1306
12 Pillai, P. K. C. and Goel, M. *Polymer* 1975, **16**, 5
13 Vanderschueren, J. and Gasiot, J. 'Thermally Stimulated Relaxation in Solids', Topics in Applied Physics, Vol. 37, Springer-Verlag, Berlin, 1979, p. 135
14 Van Turnhout, J. 'Thermally Stimulated Discharge of Electrets', Topics in Applied Physics, Vol. 33, Springer-Verlag, Berlin, 1980, p. 81
15 Bucci, C., Fieschi, R. and Guidi, G. *Phys. Rev.* 1966, **148**, 816
16 Hickmott, T. W. *J. Appl. Phys.* 1975, **46**, 2583
17 Reichle, M., Nedetzka, T., Mayer, A. and Vogel, H. *J. Phys. Chem.* 1970, **74**, 2659
18 Stupp, S. I. and Carr, S. H. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 485