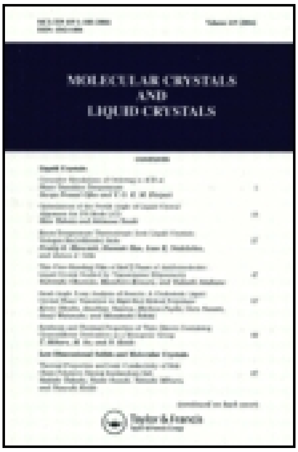

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Microstructural and Thermal Studies on Charge-Transfer Materials

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Microstructural and Thermal Studies on Charge-Transfer Materials

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Microstructural and thermal studies on charge-transfer materials have been reported in this paper. Optical microphotographs of pure donors, acceptors and their complexes have been obtained. Thermal analysis has been done to learn about their thermal stability and stoichiometries. Th solidification kinetics has been studied to learn about the role of heat treatment on these materials. Powder X-ray diffraction data and optical microphotographs have been obtained to evolve structure-microstructure – physical property correlations. It has been shown that these aspects, hitherto neglected, should be seriously pursued for developing a commercially viable process for organic electronic materials.

Keywords: Charge transfer materials, microstructure, solidification kinetics, thermal analysis, electron donors and acceptors

1. INTRODUCTION

Charge-transfer materials have been extensively studied in the recent years.[1–3] These materials have not only given us the hope of replacing the conventional inorganic electronic materials with organic ones but they have also opened the possibility of developing molecular level electronic devices.[2,4,5] Many attempts have been made to evolve structure-property correlations for organic electronic materials, but it has not been possible to arrive at a commercially viable concerted process for an organic electronic device.[5] One of the major problems has been the large variations in the reported electrical data on the same material and structurally related materials. Electrical properties of charge-transfer materials depend largely on different types of packing.[2] Segregated packing usually results in higher conductivities than alternated one due to the smaller Coulomb barriers between different states of charges on similar molecules. However, there are no controls on what type of stacking occurs except using the Langmuir-Blodgett film technology.[6]

Due to difficulties in growing large single crystals of organic materials, most of the reported literature is based on compaction of polycrystalline materials which will inherently have different grain sizes, grain boundaries etc. Thermal annealing of these materials may help in improving the reproducibility of data to some extent, but it has not been successful due to low thermal and atmospheric stabilities of these materials.

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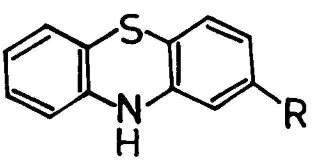
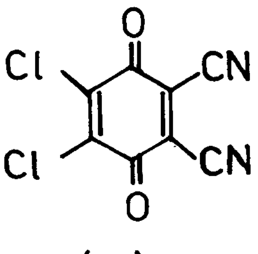
Under these experimental limitations, microstructures may be the controlling factor of the physical properties of these materials.

Surprisingly no reports are available on the microstructural studies of charge-transfer materials. Similarly, thermochemistry and solidification behaviour of these systems have not been studied. In this paper, we have attempted to look into these aspects of charge-transfer materials. We have attempted to correlate the crystallization behaviour and microstructural changes during crystallization of the charge-transfer materials with electrical behaviour. For this purpose, we have taken microphotographs of pure components like phenothiazine (I), 2-acetylphenothiazine (II), 2-chlorophenothiazine (III), 2-(trifluoromethyl)phenothiazine (IV) and 2,3-dichloro-5,6-dicyano-p-benzoquinone or DDQ (V). The microstructural studies of the charge-transfer complexes such as phenothiazine: DDQ (VI), 2-acetyl phenothiazine: DDQ (VII), 2-chlorophenothiazine: DDQ (VIII) and 2-(trifluoromethyl)phenothiazine: DDQ (IX) have been performed. The molecular structures of the electron donors, acceptor and the complexes are given below with appropriate numbering.



(I-IV)



(V)

where (I) R = H; (II) R = $-COCH_3$;
(III) R = $-Cl$; (IV) R = $-CF_3$

We have determined the linear velocity of crystallization for all the above systems except VIII and IX due to their instability at elevated temperatures. These studies have been supported by the thermogravimetric analyses of VI, VII, VIII and IX complexes. The details of the structural studies based on X-ray diffraction data and physicochemical studies of these complexes have been reported earlier.[7,8] Powder X-ray diffraction data of these charge-transfer complexes have been obtained after determining the linear velocity of crystallization. Comparison of X-ray diffraction data before and after crystallization has been made. Electrical conductivities of these materials before and after solidification on melting have been determined to evolve the microstructure-electrical property correlations.

2. EXPERIMENTAL

2.1 Materials

All the donors (I-IV) and acceptor (V) used in the present work were obtained from Aldrich Chemie. The charge-transfer complexes such as VI, VII, VIII, and IX were prepared, in general by taking appropriate amounts of the components for 1:1

stoichiometry in dicloromethane and mixing them. These charge-transfer complexes have been obtained as intense greenish black solids.

2.2 Methods and Measurements

Thermogravimetric analyses were done on Stanton Red Croft STA-780 series unit. The analytical constants were: heating rate-10°C min^{-1}; chart speed – 1000 mm/hr; reference-Al_2O_3; thermocouple-platinum-rhodium. .

The X-ray diffraction patterns were recorded on Philips X-ray diffractometer PW 1710 using CuK_α radiation.

In order to study maximum undercooling in the molten mixtures, it was necessary to know accurately the melting points of the mixtures. The undercooling was determined by keeping a small amount of the sample in the tube which was placed in oil thermostat maintained at a temperature slightly above the melting point of the material taken in the tube. When the melting of the compound was complete, the temperature of the bath was allowed to fall. This can be utilized to give a comparative estimate of undercooling for melts of different compositions.

The experimental technique for determining the linear velocity of solidification is based on the work of Rastogi and Chatterji (9). A Pyrex glass U-tube of 70 mm length and inner diameter of 4 mm was used for the measurements. This was filled with the compound for which growth velocity was to be measured. The tube was then mounted on a support fitted with a scale. The entire assembly was kept in an oil thermostat maintained at a temperature slightly above the melting point of the material taken in the tube. When the melting of the compound was complete, the temperature of the thermostat was allowed to fall at a very slow rate. A seed crystal of the same substance was added to one end of the tube for nucleation followed by crystallization. The time required for the crystal front to travel a known distance, was noted with the help of a stopwatch. Thus, the linear velocity of crystallization, i.e., the rate of movement of solid-liquid interface was determined at different undercoolings for each compound.

The samples for microstructural studies were prepared by taking a small amount of the compound on a well washed and dried glass slide, placed in an oven maintained at a temperature slightly above the melting point of the sample. On complete melting, a coverslip was glided over the melt and allowed to cool. After a few minutes, the supercooled melt was nucleated by the solid of the same composition and care was taken to have unidirectional freezing. After the complete freezing, the slide was placed on the platform of a Leitz Laborlux D, optical microscope, and different regions of the slide were examined. At suitable magnification, the microphotographs were taken with the help of a camera attached with the microscope.

Electrical conductivities were measured with the help of a Source-Measure Unit (Keithley Model 236).

3. RESULTS AND DISCUSSION

3.1 Thermal analysis

[a] Cooling Curve: A cooling curve i.e., temperature time curve for pure components is shown in Figure 1. It has been observed that after complete melting of

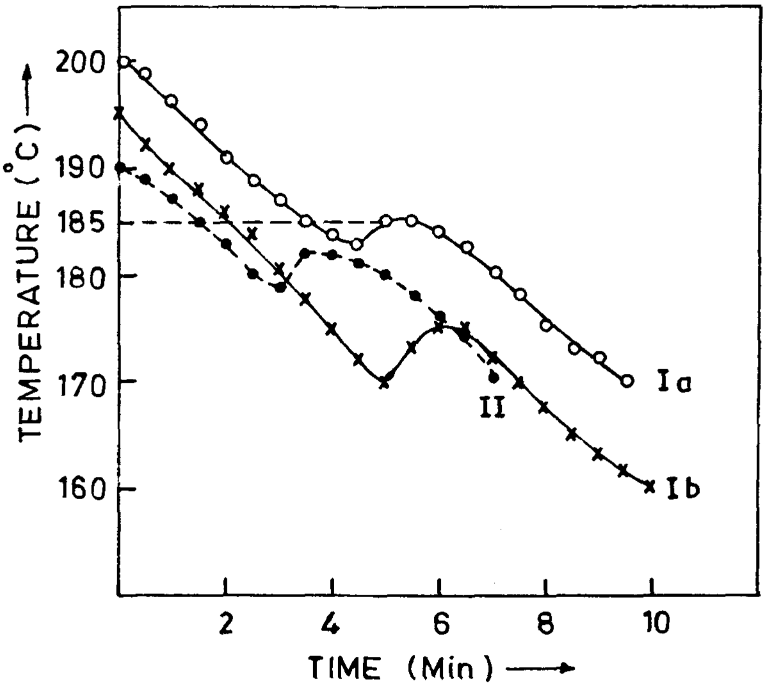


FIGURE 1 Cooling curves for phenothiazine (Ia & Ib) and 2-acetyl phenothiazine (II).

the compound, temperature was decreasing slowly with time. At a particular temperature, below the melting point, the substance had begun to solidify and temperature increased suddenly and then remained constant until all the melt was solidified. Hence, the undercoolings (ΔT) for these systems have been determined.

[b] Thermogravimetric Studies: The solid–liquid phase-diagram studies on these donor-acceptor systems have been reported earlier.[8] It has been found that these charge-transfer materials were thermally stable and stoichiometries of these materials were found to be 1:1. This stoichiometry has also been supported by their thermal analyses also. Thermogravimetric analyses of these materials are presented in Figures 2 to 5. Thermogravimetric curves show that these complexes are thermally stable upto 100°C, but undergo a two step decomposition at higher temperatures. The first step of decomposition stoichiometrically corresponds to the loss of one mole of DDQ and the second one for the loss of one mole of phenothiazines. A detailed analysis of thermogravimetric curve for complex VI (Fig. 2) shows that DDQ is lost between 130–500°C, while phenothiazine is lost from 500°C onwards. The rate of decomposition is a maximum at 280°C for V and 575°C for I as indicated in its DTG curve (Fig. 2). The DTA plot of this compound shows an endothermic peak at 169°C. Similar curves have been obtained for the complexes VII, VIII and IX, which are given in Figures 3 to 5. DTA curve of pure components show exothermic nature, while of the complexes show their endothermic behaviour.

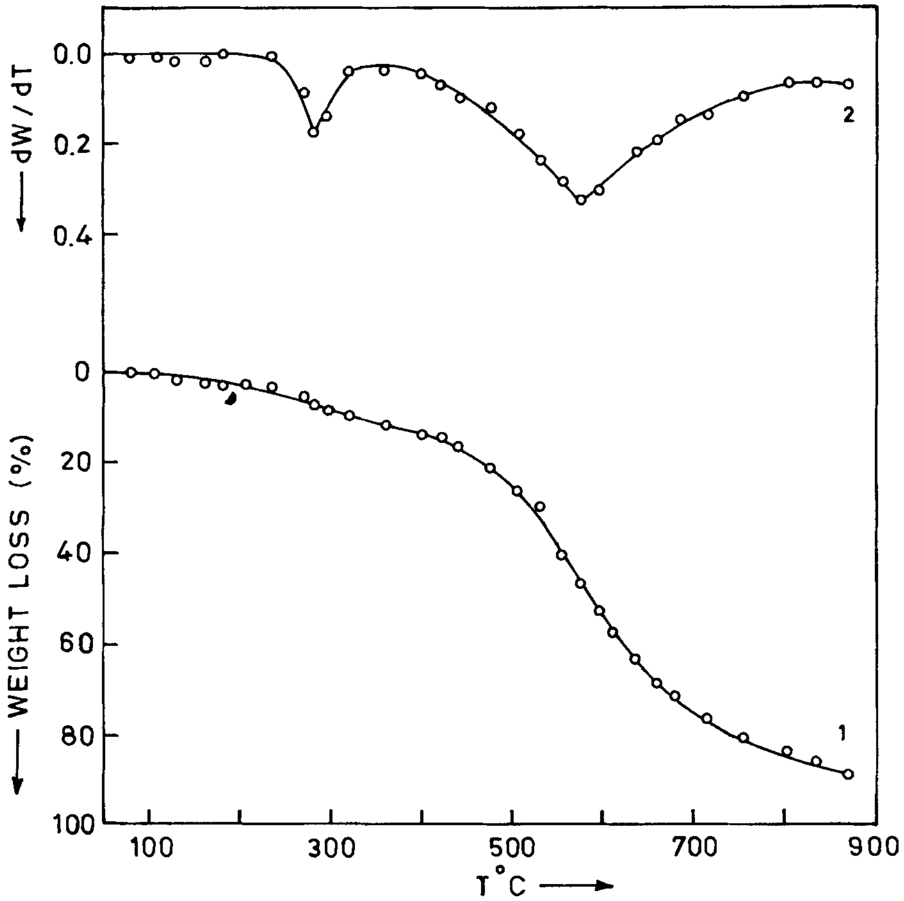


FIGURE 2 TG curve (1) and DTG curve (2) for phenothiazine: DDQ complex.

3.2 Linear Velocity of Crystallization

The linear growth velocity (V) determined by measuring the rate of movement of the crystal front at different undercoolings (ΔT) are given in Figure 6. The linear relationship between $\log V$ and $\log \Delta T$ suggests that the solidification behaviour obeys the Hillig-Turnbull Equation (10) given below.

$$V = u(\Delta T)^n$$

where, V is the linear velocity of crystallization (mm/sec). T is the undercooling in °C and u and n are constants depending upon the behaviour of solidification of the materials involved. The experimental data and the values of constants have been given in Tables I and II.

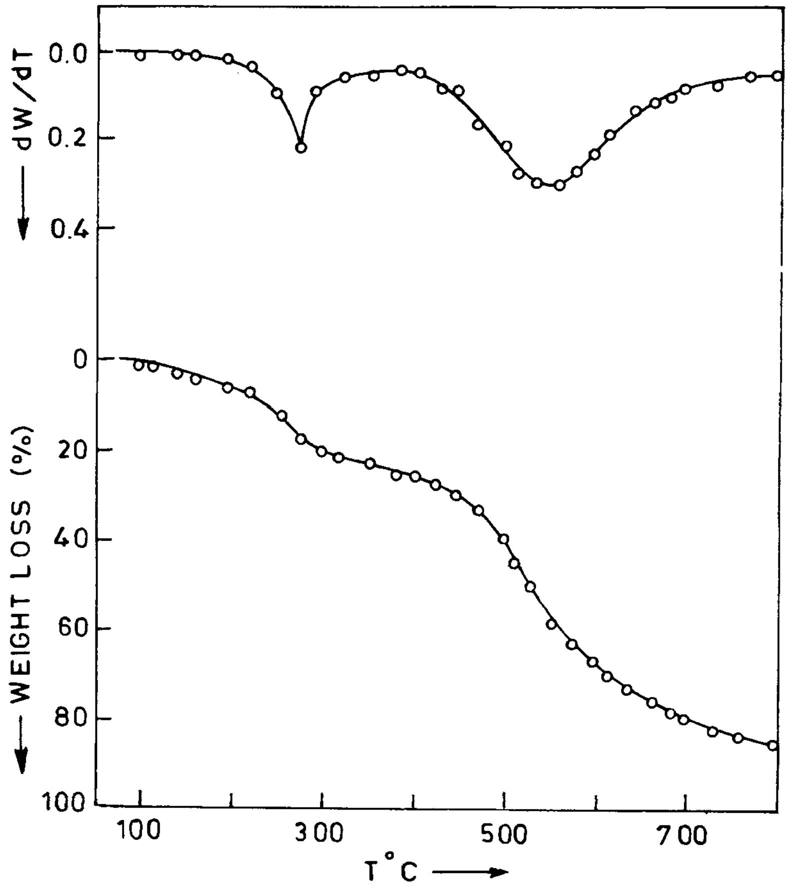


FIGURE 3 TG curve (1) and DTG curve (2) for 2-acetyl phenothiazine: DDQ complex.

According to Hillig and Turnbull's mechanism, growth occurs at the sites where the surface is particularly rough on account of lattice imperfections and screw dislocations which intersect the surfaces and produce steps of one or more molecular diameters in height. These steps are the centres of lattice disturbance and hence during growth these steps wind themselves in spirals.[11] It is evident from Figure 6 that the plots of log V vs. logΔT are straight lines whose slopes (n) are close to 2. This suggests a square relationship between the growth velocity and the undercooling. However, in some cases deviations in the values of n from 2 have been observed. When the value of n is smaller than 2, it suggests less rapid variation in the growth velocity with undercooling, while that of higher than 2, suggests more rapid variation in the growth velocity with undercooling in comparison to those observed, when $n = 2$.

From the results presented in Tables I and II, it is clear that the velocity of crystallization in charge-transfer complexes falls to much less than the value of the velocity of crystallization of donor components. It has also been observed in the crystallization of melts of various mixtures of naphthalene and phenanthrene.[11] The

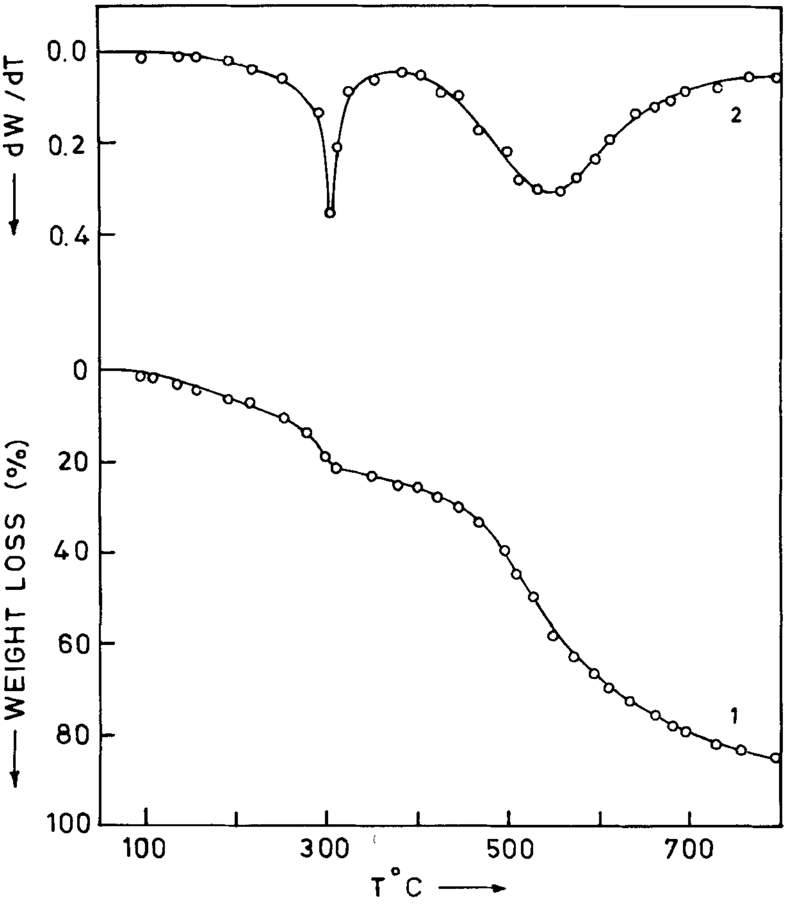


FIGURE 4 TG curve (1) and DTG curve (2) for 2-Chlorophenothiazine: DDQ complex.

low value of velocity is primarily due to the low value of the constant which depends on the frequency of impacts on the moving boundary. Clearly, the frequency of successful impacts of the separating component in a mixture can never be of the same order as in the melt of a pure component. Our results can be explained on the basis of the mechanism proposed by Winegard *et al.*[12] The solidification begins with the formation of a nucleus of one of the phases. This would grow until the surrounding liquid becomes rich in the other component and a stage is reached when the second component starts nucleating. Now there are two possibilities. First, the two initial crystals may grow side by side. The second possibility is that there may be alternate nucleation of the two components. In our case the second possibility is observed. It has been found that although the limit of undercooling for pure components like I and II and the charge-transfer complexes like VI and VII are of the same order, the linear velocity of crystallization of the charge-transfer materials is much lower than that of the pure components possibly due to alternate nucleation of the parent components.

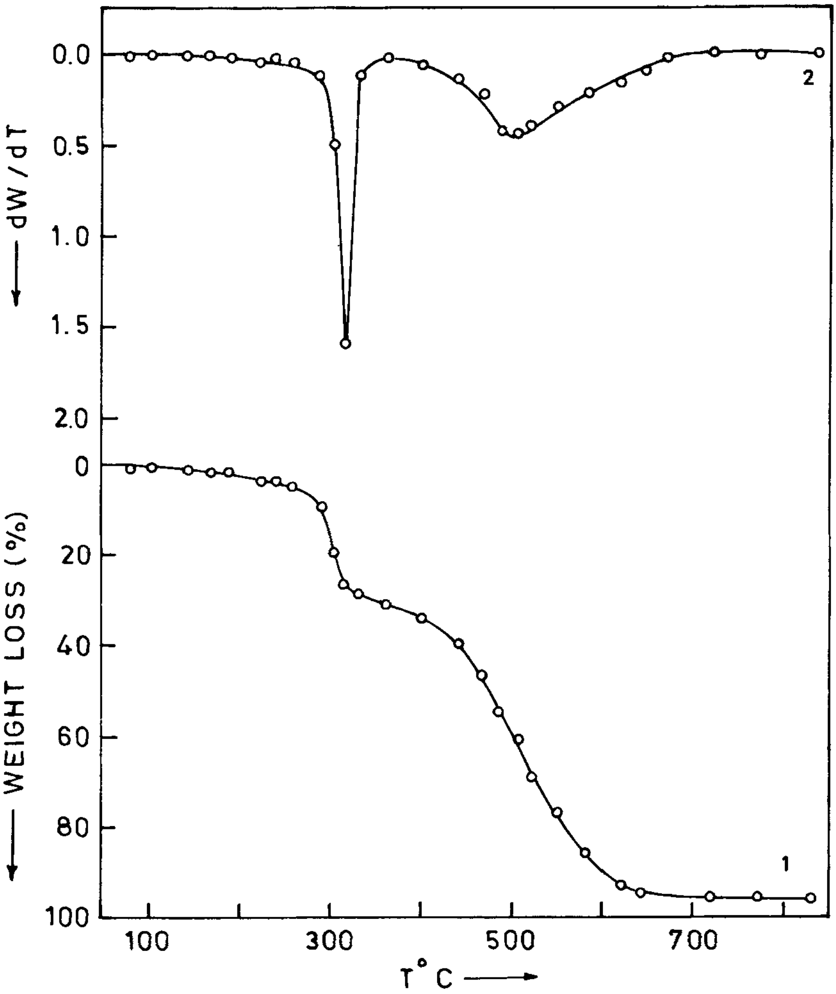


FIGURE 5 TG curve (1) and DTG curve (2) for 2-(trifluoro) methyl phenothiazine: DDQ complex.

3.3 Microstructural Studies

The optical microphotographs of pure donors and acceptors and their complexes have been shown in Figures 7 to 10. The microstructures of I, III and IV are of cellular type (Fig. 7). However, three different types of microstructures have been obtained for II (Fig. 8). In Figure 8a, microstructure appears to have a lamellar structure with radial growth. On microscopic scale nodules consist of lamellae radiating outwards from their centre and growing approximately normal to solid-liquid phase. Figure 8b shows that the microstructure consisting of three boundaries meeting at one place in regular fashion. At *x* 600 magnification of one portion of the microstructure of II, lamellar structure could be seen (Fig. 8c). Microstructure of acceptor DDQ (V), shown in

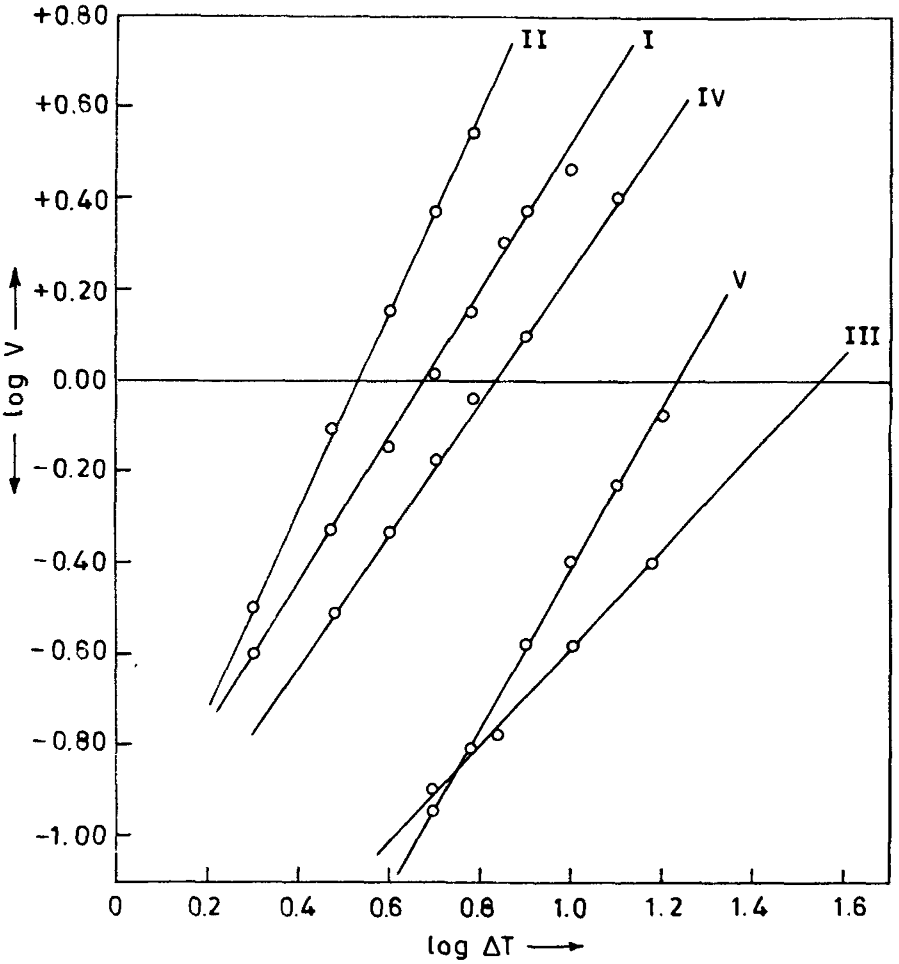


FIGURE 6 Linear velocity of crystallization curves for phenothiazine (I), 2-acetylphenothiazine (II), DDQ (III), phenothiazine: DDQ complex (IV) and 2-acetylphenothiazine: DDQ complex (V).

Figure 8d and e is of lamellar type in regular fashion. The lamellar phase tends to grow normal to the solid–liquid interface, which, because of the co-operative nature of the growth process, remains approximately planar on the scale of the lamellar widths.

The microstructure of the charge-transfer materials studied is irregular and colony type. The optical microphotographs of the complexes VI and VIII are given in Figure 9, which show complexed and colony type micro-structures. Microphotographs of VII and IX are shown in Figure 10. Microstructure of the complex VII shows dark spots intersected in the white background. Similar microstructures for different compounds have been reported by Chadwick.[13] Comparison of all these microstructures shows

TABLE I

Linear Velocity of Crystallization and Values of Constants *u* and *n* for Parent Component

Compounds	Under-coolings *T* (°C)	log Δ *T*	Crystallization velocity *V* (mm/sec.)	log *V*	Values of *u* (mm $sec^{-1} deg^{-1}$)	Values of *n*
I (m.p. 184–186°C)	2	0.30	0.2500	−0.60	0.01230	1.7
	3	0.48	0.4667	−0.33		
	4	0.60	0.7000	−0.15		
	5	0.70	1.0000	0.0		
	6	0.78	1.4000	+0.15		
	7	0.85	2.0000	+0.30		
	8	0.90	2.3333	+0.37		
	10	1.00	2.8000	+0.45		
II (m.p. 185–186°C)	2	0.30	0.3182	−0.50	0.01480	2.2
	3	0.48	0.7778	−0.11		
	4	0.60	1.4000	+0.15		
	5	0.70	1.3333	+0.37		
	6	0.78	3.5000	+0.54		
V (m.p. 205–207°C)	5	0.70	0.1250	−0.90	0.04467	1.4
	7	0.85	0.1667	−0.78		
	10	1.00	0.2632	−0.58		
	13	1.11	0.3333	−0.48		
	15	1.18	0.4000	−0.4		

TABLE II

Linear Velocity of Crystallization and Values of Constants *u* and *n* for Complexes

Compounds	Under-coolings T (°C)	$\log \Delta T$	Crystallization velocity V (mm/sec.)	$\log V$	Values of u (mm $\sec^{-1} \deg^{-1}$)	Values of n
VI (m.p. 270–275°C)	3	0.48	0.3125	−0.51	0.00166	1.5
	4	0.60	0.4545	−0.34		
	5	0.70	0.6666	−0.18		
	6	0.78	0.9091	−0.04		
	8	0.90	1.2500	+0.10		
	10	1.00	1.6667	+0.22		
	13	1.11	2.5000	+0.40		
VII (m.p. 170–175°C)	5	0.70	0.1111	−0.95	0.00130	1.8
	6	0.78	0.1538	−0.81		
	8	0.90	0.2632	−0.58		
	10	1.00	0.4000	−0.40		
	13	1.10	0.5882	−0.23		
	16	1.20	0.8333	−0.08		

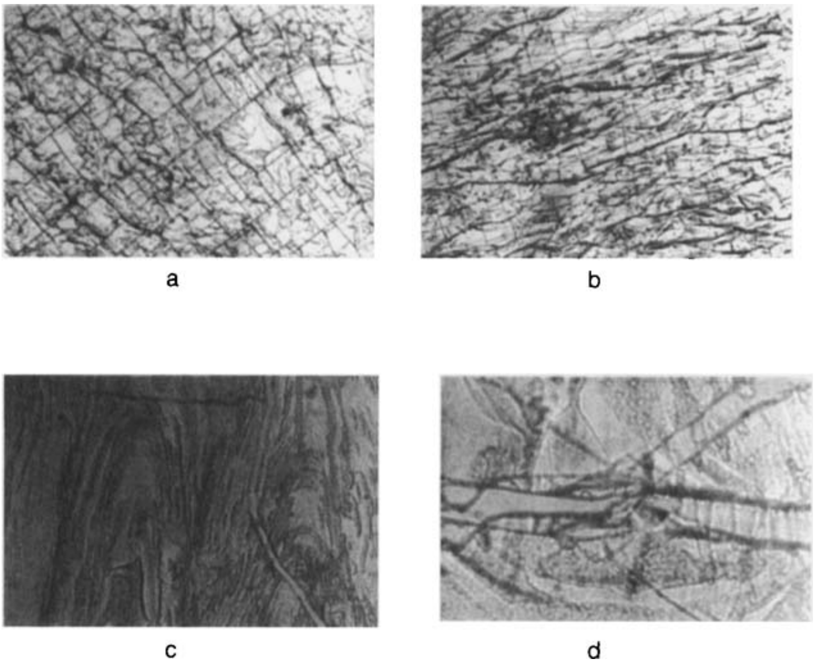


FIGURE 7 Microphotographs of different compounds (a) phenothiazine at × 100 magnification; (b) 2-(trifluoro) methyl phenothiazine at × 100 magnification; (c) and (d) 2-chlorophenothiazine at × 100 magnification.

that the crystallization of the charge-transfer materials, has altogether different characteristics, having complexed nature as compared to the parent component possibly due to additional charge-transfer interactions between donors and acceptors.

3.4 X-Ray Diffraction Data

The powder X-ray diffraction data on the charge-transfer complexes of phenothiazines with DDQ before solidification through heat-melt method have been reported earlier.[7] The X-ray diffraction data of these charge-transfer materials after solidification on melt have also been obtained for comparison. The lattice parameters for different complexes before and after solidification on melt are as follows:

Before solidification
[a] VI: *a* 6.020 Å, *b* 9.775 Å, *C* 24.280 Å
[b] VII: *a* 5.055 Å, *b* 7.955 Å, *C* 19.520 Å

After solidification
[a] VI: *a* 5.910 Å, *b* 7.900 Å, *C* 21.000 Å
[b] VII: *a* 5.920 Å, *b* 7.600 Å, *C* 24.640 Å

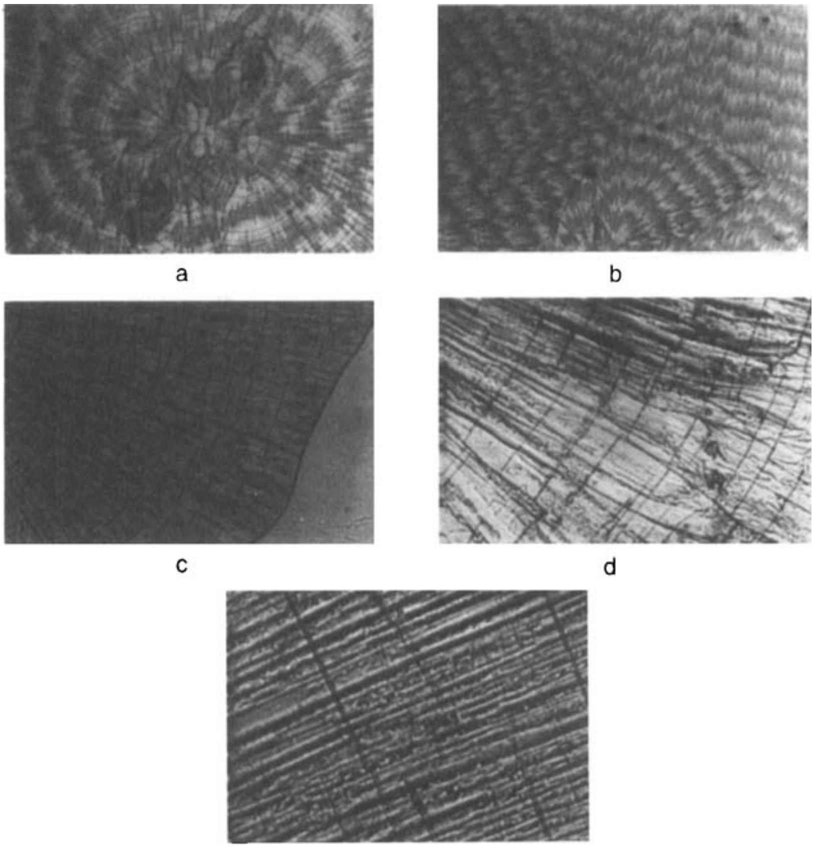


FIGURE 8 Microphotographs of different compounds (a) and (b) 2-acetylphenothiazine at × 100 magnification; (c) 2-acetylphenothiazine at × 600 magnificaton; (d) DDQ at × 100 magnification and (e) DDQ at × 600 magnification.

The above data indicate that the solidification of the charge-transfer materials through heat-melt method changes the lattice parameters to some extent but the crystal structure remains the same (Orthorhombic) before and after solidification from the melt.

Structure – Property Correlations

The infrared spectral data, presented in Table III indicate that there is no change in absorption frequencies before and after solidification. The characteristic bands for different species have been obtained as reported earlier.[8] This suggests that the chemical nature of different species remains the same even after solidification from melt at different undercoolings. Similarly, the crystal structures remain orthorhombic during the process but there is slight change in the lattice parameters. However, the electrical conductivities of compacted polycrystalline materials before and after solidification show a variation of a factor of ten to twenty being more in the

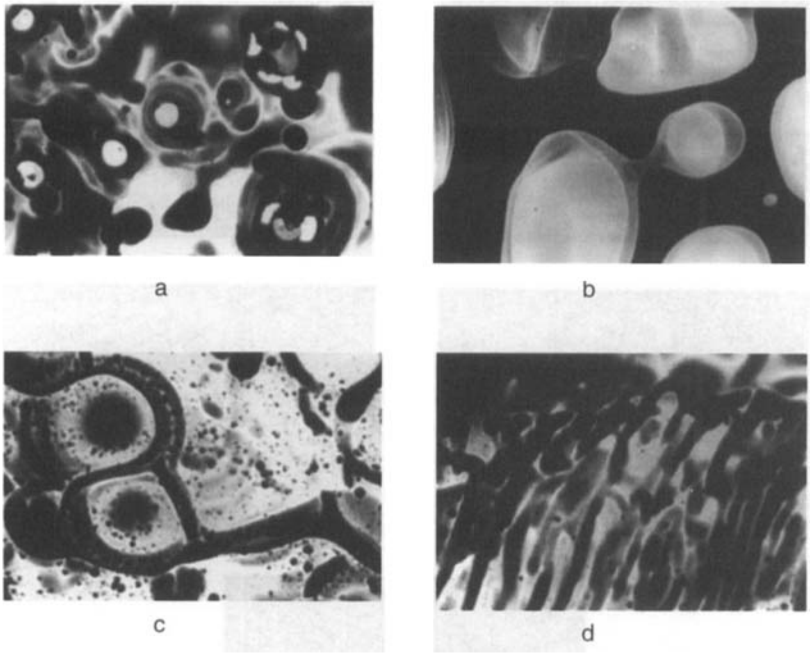


FIGURE 9 Microphotographs of different complexes (a) and (b) phenothiazine: DDQ at × 100 magnification; (c) and (d) 2-chlorophenothiazine: DDQ at × 100 magnification.

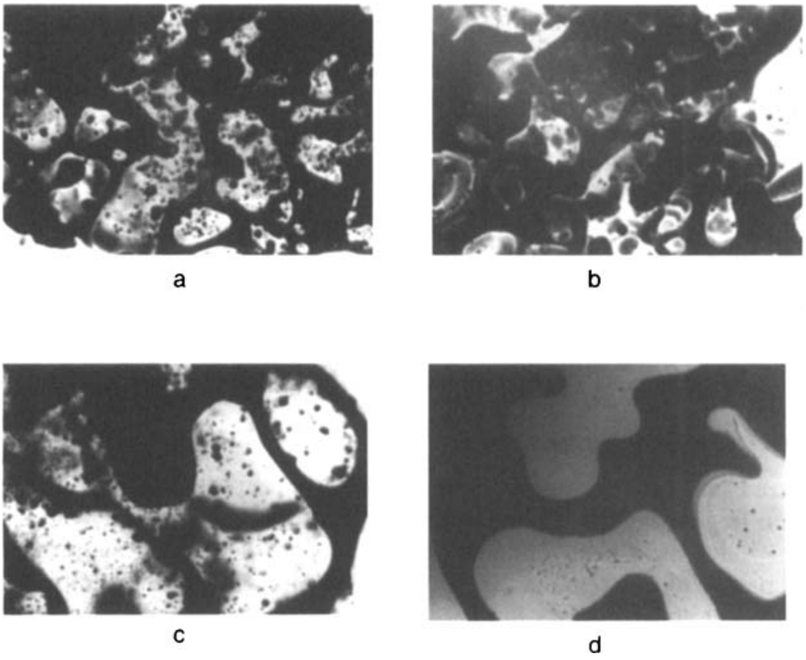


FIGURE 10 Microphotographs of different complexes (a) and (b) 2-acetylphenothiazine: DDQ at × 100 magnification; (c) and (d) 2-(trifluoro) methyl phenothiazine: DDQ at × 100 magnification.

TABLE III

Selected infrared spectral bands (cm^{-1}) of the parent components and the charge-transfer complexes in KBr before and after crystallization on melts

Compounds	I R bands (cm^{-1})				
	$\nu_{(N-H)}$	$\nu_{(>C=O)}$	$\nu_{(C\equiv N)}$	$\nu_{(semiquinoneion)}$	$\nu_{(aromatic)}$
(Before crystallization)					
I	3341.01	—	—	—	1597.20, 1572.13, 1473.75,
II	3346.80	1668.58	—	—	1560.55, 1467.96
V	—	1676.29	2363.01, 2233.77	—	—
VI	—	—	2363.01	3412.38, 1228.77, 1124.60	1572.13
VII	—	1670	2363.01	3412.38, 1228.77, 1124.60	1572.13
(After crystallization)					
I	3341.01	—	—	—	1597.20, 1572.13, 1473.75,
II	3346.80	1666.65	—	—	1562.48, 1469.89
V	—	1676.29	2363.01,	—	—
VI	—	—	2363.01 2253.06	3244.56, 1275.06, 1190.19	1575.98
VII	—	1665	2363.01 2253.06	3227.20, 1275.06, 1192.12	1560.55

former than in the later case. The values of electrical conductivities at r.t. are given as follows:

Before solidification
VI : 26.37 nScm^{-1}
VII : 74.28 nScm^{-1}

After solidification
VI : 0.80 nScm^{-1}
VII : 12.60 nScm^{-1}

This may be due to the fact that the thermal treatment of the material results in ordered but alternated mixed stacked donors and acceptors as proposed earlier[8] in which it is more diffcult to transport charge via unlike molecular species having higher Coulomb barriers. Heat treatment of these organic materials generates complex cellular microstructures having large grain boundaries which also inhibit charge transport through these materials. It is concluded that the microstructure of charge-transfer materials play an important role in governing the physical properties of these materials. Further, work on a variety of other systems is in progress and will be reported later.

4. CONCLUSION

The results presented in this paper open a new direction of research on charge-transfer materials, particularly with the interest of developing commercially viable processes for organic electronic materials. Thermal analysis, solidification kinetics and microstructure indicate that the heat treatment, rate of solidification and resulting microstructure play a major role in the physical properties of these materials.

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References

1. F. Gutmann and L. E. Lyons in *Organic Semiconductors*, John Wiley and Sons Inc., New York, 1967.
2. R. C. Haddon, M. L. Kaplan and F. Wudl in *Encyclopaedia of Semiconductor Science and Technology* ed. by M. Grayson, New York, 1984.
3. J. B. Torrance, *Mol. Cryst. Liq. Cryst.*, **126**, 55 (1985).
4. J. Simson and J. J. Andre in *Molecular Semiconductors* ed. by J. M. Lehn and Ch. W. Rees, Springer-Verlag, New York, 1985.
5. G. J. Ashwell (ed.) in *Molecules Electronics*, Research Studies Press Ltd., Taunton, England, 1992.
6. G. G. Roberts (ed.) in *Langmuir-Blodgett Films* Plenum Press, New York, 1982.
7. R. A. Singh, R. Singh and S. M. Verma, *Cryst. Res. Tech.*, **26**, 201 (1991).
8. R. A. Singh, R. Singh and S. M. Verma, *Indian J. Techn.*, **29**, 241 (1991).
9. R. P. Rastogi and A. C. Chatterji, *J. Phys. Chem.* **59**, 1 (1955).
10. W. B. Hillig and D. Turnbull, *J. Chem. Phy.*, **24**, 914 (1954).
11. R P. Rastogi and P. S. Bassi, *J. Phys. Chem.*, **68**, 2398 (1964).
12. W. C. Winegard, S. Majka, B. M. Thall and B. Chalmers, *Can. J. Chem.*, **29**, 320 (1951).
13. G. A. Chadwick (ed.) in *Metallography of Phase Transformations*, Butterworth and Co. Ltd., London (1972).