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Mechanical properties of conducting poly(3-cyclohexyl thiophene) films

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Poly(3-cyclohexyl thiophene) was prepared and made into films. Tensile properties of these films were studied at various temperatures. The draw ratio was maximum around 55°C. The results show that flow and orientation take place in the material around this temperature due to a primary transition. The stiffness and tensile properties were very much affected due to the bulk cyclohexyl substitution at the 3 position. Copyright © 1996 Elsevier Science Ltd.

(Keywords: conducting polymers; polyalkyl thiophenes; mechanical properties)

INTRODUCTION

Electrically conducting conjugated structures form a group of speciality polymers having high utility. These materials have versatile application potentials in antistatic coating, electro magnetic shielding, micro electronics, energy storage, electro catalytic systems, photo voltaic devices, electrochromic devices etc. Conjugated polymers are often insoluble and infusible because of their chain stiffness and relatively strong interchain interactions. In the case of polymer to be potentially useful in electronic applications, a material must have excellent electrical and mechanical properties. It should be either a solution or a melt-processible material with high environmental stability.

Studies[1-3] have shown that solubility can be achieved through the addition of appropriate side groups. Poly(3-alkyl thiophenes) having side chain lengths greater than four carbon atoms are soluble in a variety of solvents and are fusible, thus they can be easily processed. Considerable work has been done in improving the 3-substituted polythiophene polymer synthesis[4-6]. A broad range of mechanical and electrical properties can be obtained through the variation of the alkyl chain length[7,8]. The melt processibility/stretching under increased temperature of poly(3-alkyl thiophene) has allowed for the introduction of chain alignment and extension, improving the mechanical and electrical properties of the films[7,9]. At a temperature, at which maximum stretching was obtained, the mechanical and electrical properties show high values. In this present work we report the effect of temperature on the mechanical properties and tensile fracture behaviour of poly(3-cyclohexyl thiophene) polymer films.

EXPERIMENTAL

The 3-cyclohexyl thiophene monomer[9] was prepared by a cross coupling reaction between cyclohexyl magnesium bromide and 3-bromo thiophene in dry diethyl ether containing a nickel catalyst following the method described by Kumada *et al.*[11]. The monomer was subsequently purified by chromatography on flash gel using n-heptane as eluent and finally distilled under reduced pressure at 0.1 mbar and 55°C.

Chemical polymerization

Poly(3-cyclohexyl thiophene) (P3c6T) was prepared by chemical oxidation of the monomers using $FeCl_3$ adopting a procedure similar to that of Sugimoto *et al.*[5]. The polymer obtained from the reaction was washed with methanol and acetone and finally dried under reduced pressure at 50°C.

Film formation

The P3c6T polymer was dissolved in chloroform in an amber coloured-bottle and filtered using a membrane filter, Millipore type FH 0.5 μm. The filtrate was dried in the dark in order to avoid photodegradation and made into film using a flat glass Petri dish. The dried film was conditioned in a desiccator for 3 days at 65% r.h. and at 25°C. Stress–strain characteristics of these films were studied using an Instron universal tensile tester (model 1112) with a thermostatic test chamber surrounding the specimen and grips. Testing at different temperatures was done by adopting the procedure discussed in our earlier publication[12]. The samples were tested at a rate of elongation of 100% min^{-1}. The sample gauge length was 10 mm. The modulus, stress and strain at break were measured and reported as the average of at least four measurements.

Morphology of the tensile fractured samples (fracture

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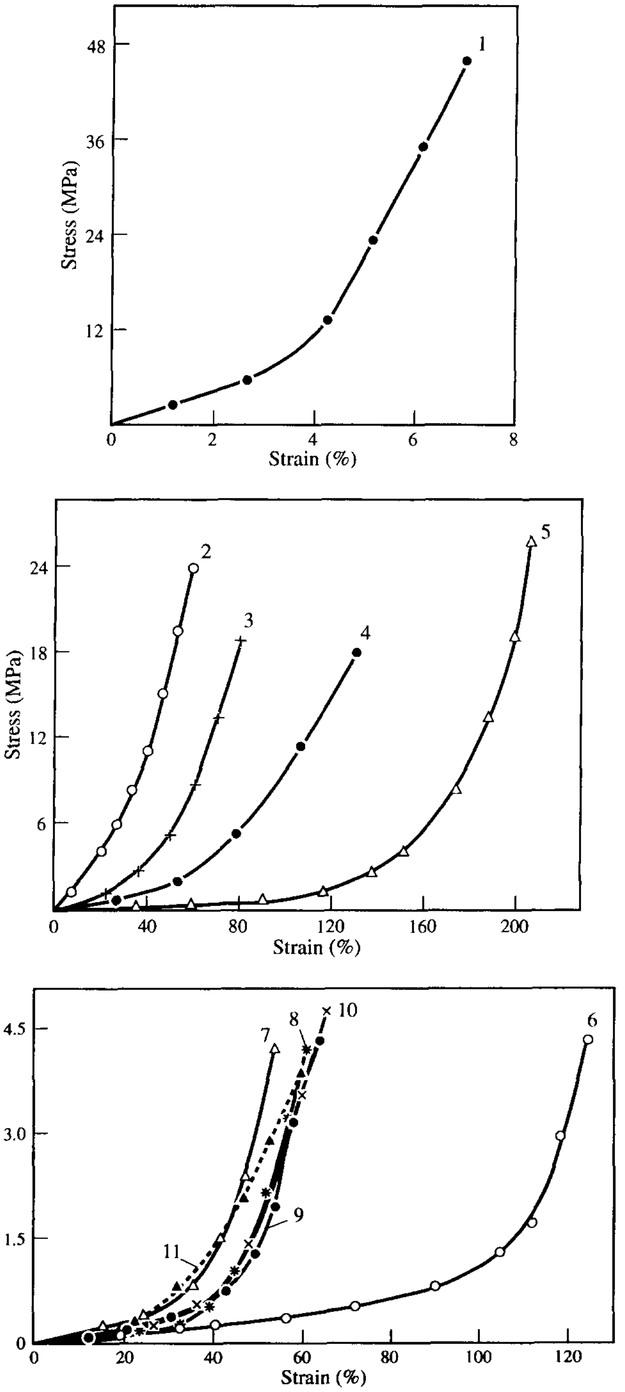


Figure 1 Stress–strain behaviour of P3c6T films at different temperatures (°C): 1—28; 2—37; 3—43; 4—49; 5—55; 6—67; 7—75; 8—90; 9—121; 10—140; 11—150

edge and fracture surface) were studied using Stereo Scan S-150 scanning electron microscope.

RESULTS AND DISCUSSION

The stress–strain characteristics of P3c6T films at different temperatures are presented in *Figure 1* (*Table 1*)[13]. At room temperature, initially the rate of variation in stress is less with the increase in strain, and after the pseudo yield point[14], which occurs at 4.25% extension, the stress sharply increases. Comparison of stress–strain behaviour of neutral polythiophene[15] with that of P3c6T, clearly indicates that the stiffness and strength was very much affected due to the substitution of cyclohexyl group at 3 position of the ring.

Table 1 Effect of temperature on tensile properties

Temperature (°C)	Stress at break (MPa)	Strain at break (%)	σ_y/σ_b (%)	E_y/E_b (%)
25	43.96	7.0	30.71	60.71
37	22.84	58.7	36.12	56.26
43	17.97	80.0	29.22	62.50
49	17.07	131.0	30.76	59.54
55	24.12	206.0	34.20	83.98
67	3.91	122.6	46.04	91.80
75	4.06	53.0	36.94	79.25
90	4.00	60.0	33.79	75.00
121	4.18	63.3	30.84	78.99
140	4.80	65.0	28.75	73.85
150	3.99	59.6	39.89	72.15

σ_y—stress at yield; σ_b—stress at break;
E_y—strain at yield; E_b—strain at break

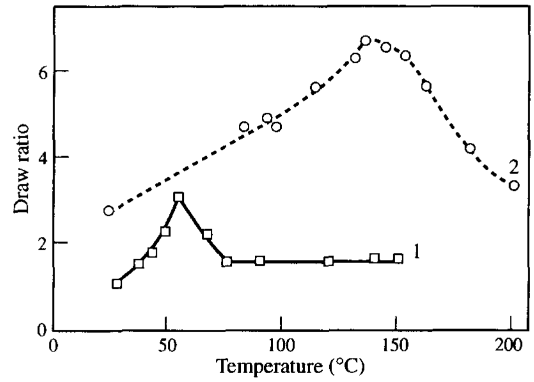


Figure 2 Effect of temperature on draw ratio. 1—P3c6T; 2—P36T (from ref. 7)

In the case of polythiophene films, there is a well-defined yield point, obtained at very low yield stress values[15]. Whereas in P3c6T films, the stress at yield is very low. Low stiffness has also been previously observed for rigid polymers, which were also solubilized through the attachment of long alkyl chain[16,17]. In the case of P3c6T, the low stress values both at yield and at break, when compared with unsubstituted polythiophene, is due to both (a) dilution by the alkyl groups of the number of load bearing covalent bonds per unit cross section and (b) reduction in secondary bond interaction[7].

Figure 1 shows that the stress decreases with the increase of temperature, whereas the strain value increases. In all the cases, with the increase of strain the increase in stress is initially low and, after a pseudo yield point, the stress suddenly increases. With the increase of temperature the stress–strain curve moves towards the strain axis. In *Figure 2* the effect of temperature on draw ratio is presented. With the increase of temperature, draw ratio increases to a maximum value of 3.1 and then decreases. After 75°C there is no characteristic variation and the draw ratio value levels off. Moulton and Smith[7] reported the temperature–draw ratio relation for poly(3-n-hexyl thiophene) (P36T), poly(3-octyl thiophene) (P38T) and poly(3-dodecyl thiophene) (P3-12T). Comparison of the results obtained for the above polymers clearly suggests that, as the side chain length decreased, higher thermal energy (temperature) was required to achieve the maximum

Table 2 Energy values obtained from stress–strain curves

Temperature (°C)	Energy to break (MJ m^{-3})	Energy to yield (MJ m^{-3})	Post-yield energy (MJ m^{-3})
25	1.031	0.206	0.825
37	5.175	1.725	3.450
43	4.455	1.680	2.775
49	7.275	1.380	5.895
55	7.845	2.580	5.265
67	0.873	0.516	0.357
75	0.501	0.158	0.343
90	0.471	0.107	0.364
121	0.533	0.176	0.357
140	0.662	0.174	0.488
150	0.650	0.183	0.467

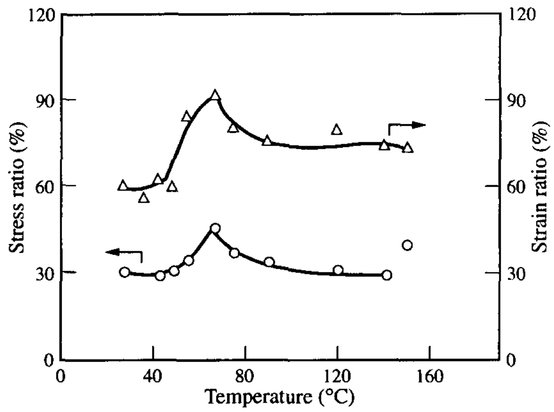


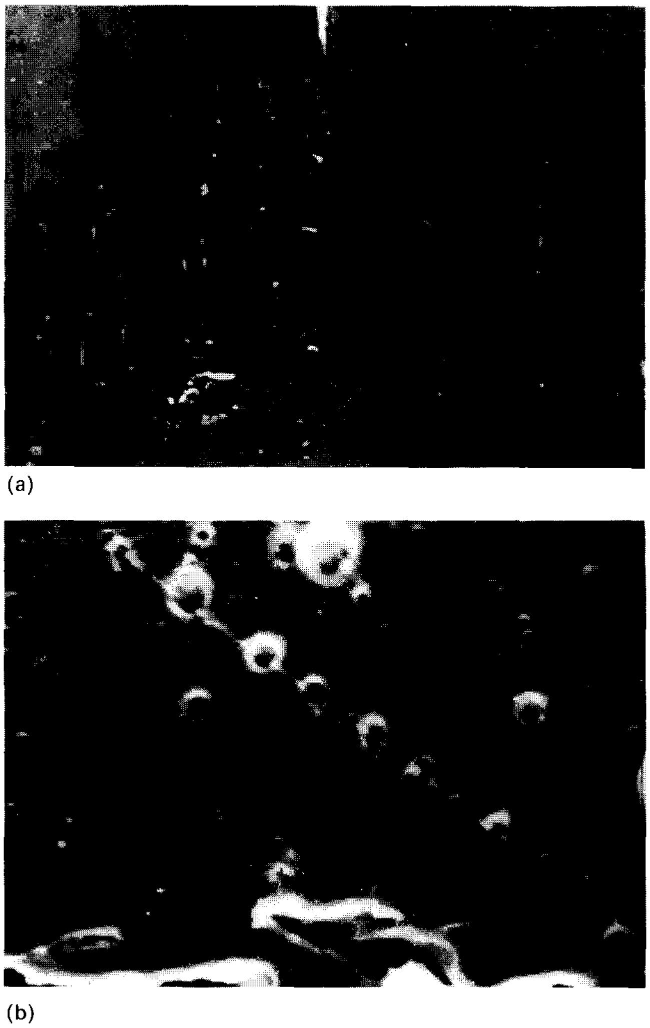
Figure 3 Effect of temperature on stress ratio and strain ratio

draw ratio, due to the effect produced by alkyl chains. In the case of P3c6T, the optimum deformation temperature ($T_{\mathrm{y\,max}}$) was lowered, due to the substitution of the bulky cyclohexyl group, the anisotropy in the material produced due to regiospecificity and the alkyl chain. This value is even lower than that of $T_{\mathrm{y\,max}}$ for P3-12T, having 12 carbon atoms.

Due to the above-mentioned effects, the maximum draw ratio obtained was also reduced to 3.1, whereas in the case of P36T, the maximum draw ratio was 6.7[7].

The energy-to-break, yield energy and post-yield energy at different temperatures are given in *Table 2*. The energy-to-break increases with the increase of temperature to a maximum at 55°C and then decreases to a minimum value and levels off. After 75°C, there is not much variation in the energy needed to break the sample. Like total energy-to-break, the energy-to-yield and post-yield energy also follow the same trend, showing a maximum at 55°C and then levelling off.

Effects of temperature on stress-at-yield/stress-at-break (stress ratio) and strain-at-yield/strain-at-break (strain ratio) are presented in *Figure 3*. The stress ratio increases to a maximum value at 67°C and then decreases, whereas there was no characteristic change in the strain ratio. Up to 55°C and after that point it increases to a maximum value of 91% at 67°C. After 67°C it decreases and levels off. Energy-to-break results suggest that the sudden increase in energy was spent to draw the sample to high yield strain. With the increase of temperature, the molecular relaxation[7] becomes significantly more rapid and, therefore, the sample yields to higher strain. After the transition point, the strain and stress ratios also decrease, since the relaxation was also reduced.


(a)

(b)

Figure 4 Fracture morphology of P3c6T film at 25°C. (a) Fracture surface (500×); (b) fracture edge (1000×)

The fracture surface and fracture edge morphologies of the P3c6T samples, fractured at different temperatures, were analysed using scanning electron microscopy. The fracture edge and surface morphologies of the films at 25°C are presented in *Figure 4*. Fracture edge morphology suggests that the fracture in P3c6T at 25°C is of brittle type and the fracture takes place by crazing mechanism. *Figure 4a* shows the magnified view of craze lines and the crack propagates perpendicular to the fracture edge. During stretching, microvoids are formed at weaker points. The cracks propagate through these microvoids (*Figure 4b*), join together, and the material abruptly fails even under low stretching condition.

In *Figure 5*, the fracture surface and fracture edge morphology of P3c6T at 55°C is presented. The fracture surface shows that at 55°C, the material has flown and has oriented in the direction of stress application. The occurrence of failure and the crack propagation is similar to that at room temperature. But due to flow and orientation, the voids also orient and become elliptical in shape and the material in between the voids shows highly oriented structure. Due to orientation, the material shows higher stress and strain values at break (*Table 1*). The fracture edge clearly shows that the material has

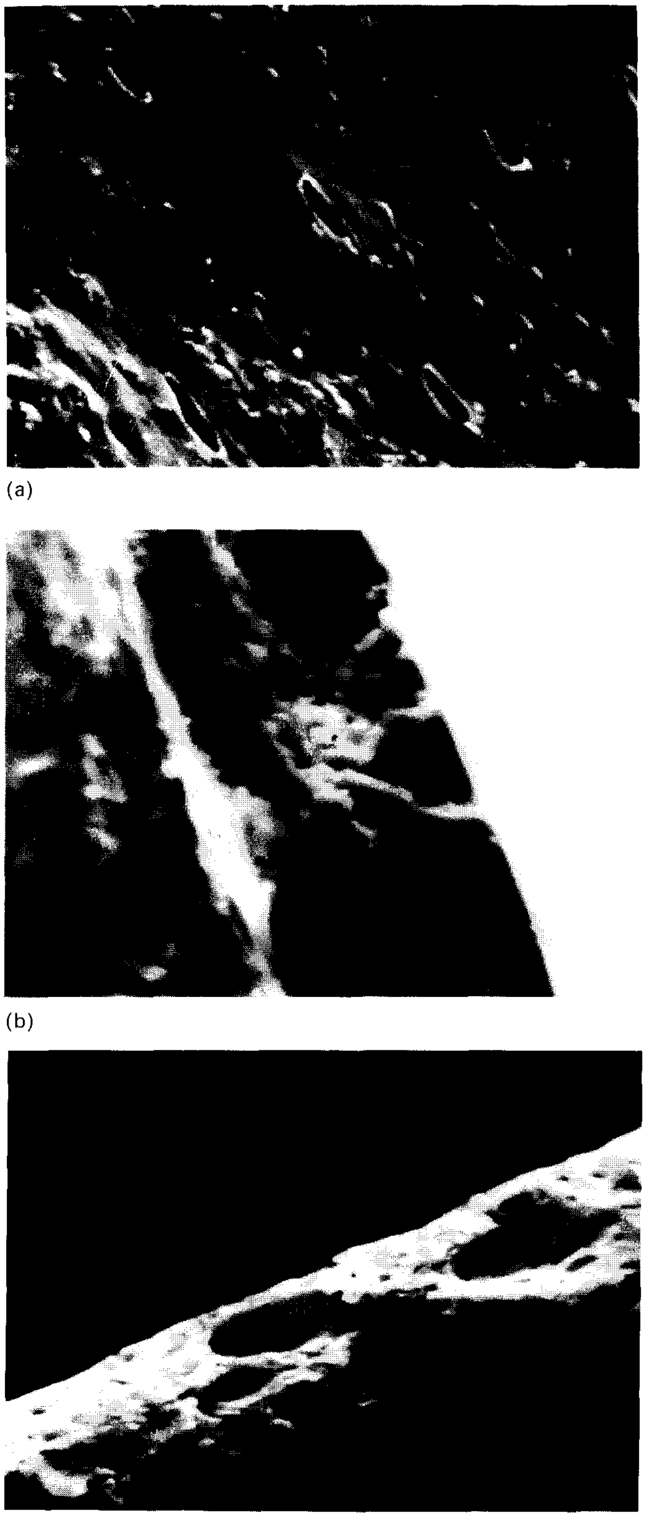


Figure 5 Fracture morphology of P3c6T film at 55°C. (a) Fracture surface (500×); (b, c) fracture edge, (b) 1000×; (c) 1000×

flown in the direction of the neck and the cross sectional thickness has considerably reduced (*Figure 5c*). The flow was towards the neck point. Comparison of fracture edge morphology of P3c6T at 25 and 55°C clearly shows that in the former case the failure is of brittle type, while in the latter case it is a ductile fracture. The failure occurs in the material after the formation of a neck.

The fracture morphology of P3c6T at 120°C is shown in *Figure 6*. The morphology shows that at 120°C, due to stress application, neck formation and orientation take place in the material. The level of orientation at 120°C is less than that at 55°C. Morphological studies clearly show that at 55°C, due to very high orientation produced at this temperature, the material forms into a compact structure and hence the high strength and stretch at this temperature. Conductivity of drawn P3c6T films was studied after doping it with iodine. The results (*Table 3*) suggest that drawing improves the electrical conductivity of P3c6T films by factor of seven, when compared with unstretched film. This is similar to the trend reported by other workers[7,18–21]. The results suggest that both conductivity and tensile strength are strongly affected by both inter- and intra-chain interactions[22]. Comparison of conductivity results of P3c6T with P36T[7] suggest that the effect produced by drawing is very much pronounced in the case of P3c6T.

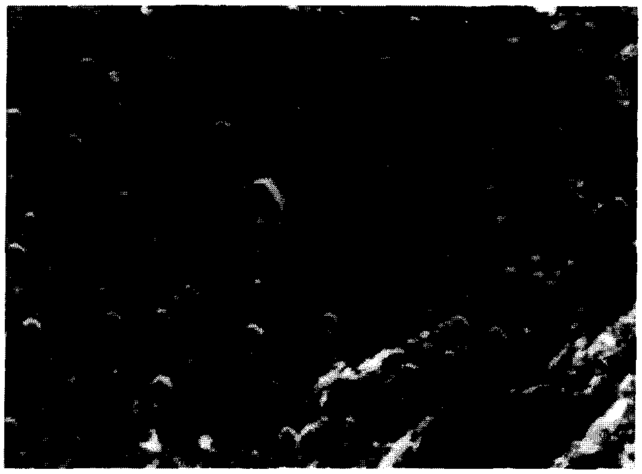


Figure 6 Fracture surface morphology of P3c6T film at 120°C (1000×)

Table 3 Conductivity of drawn P3c6T film after doping (S cm^{-1})

Draw ratio	Conductivity $\times 10^{-4}$
1	2.41
1.8	4.29
3.0	17.38

During polymer formation, the structural defects and therefore the anisotropy were increased in P3c6T, when compared with P36T[10]. Drawing reduces anisotropy present in the polymer and enhances the properties. In P36T, the increase in conductivity was only four times for a draw ratio of 5, whereas in P3C6T, even for a draw ratio of 3, conductivity was improved by a factor of seven. The results suggest that mechanical drawing decrease anisotropy of P3c6T polymer.

The above-mentioned studies on mechanical and morphological aspects of P3c6T at different temperatures clearly show that a primary transition occurs around 55°C in the material. Due to this, brittle–ductile transition takes place in the material and the film orients and form into a compact structure.

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