

# The $\beta$ -loss process in liquid crystal polyesters containing 2,6-naphthyl groups

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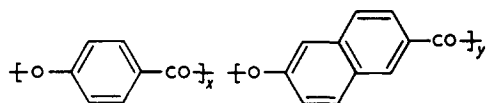
Dielectric and mechanical loss processes have been measured on a group of three polyesters containing 2,6-naphthyl groups in which the bordering ester linkage is joined to the naphthalene group in different ways. Systematic absences of the dielectric  $\beta$  loss process at about 50°C indicate that the process is associated with the naphthyl groups and neighbouring carbonyl groups undergoing a coordinated rotation motion about the main polymer axis.

(Keywords: naphthyl/phenyl copolyesters; thermotropic; dielectric loss; dynamic mechanical analysis)

## INTRODUCTION

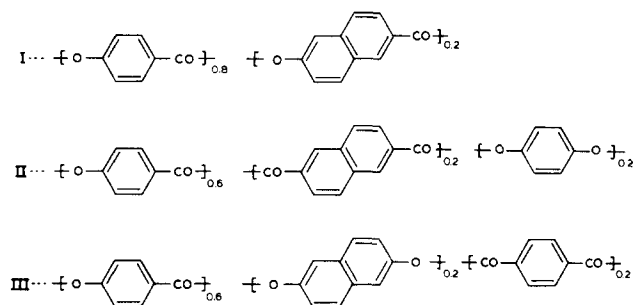
Rigid chain thermotropic liquid crystal polymers made from random naphthyl and phenyl esters exhibit some sharp X-ray diffraction peaks which can be interpreted as being associated with regions with a low degree of three dimensional order<sup>1</sup>. On heating, these peaks disappear over a temperature region where simultaneously the mechanical rigidity is lost and where there is also a small d.s.c. melting endotherm. The ordered regions therefore appear to play a similar role to crystals in conventional polymers in that they tie the molecules together and impart mechanical rigidity. However the crystallites in these liquid crystal polymers only account for a minor proportion of the total material. The remaining material although conforming to a general nematic configuration possesses no three dimensional correlation between segments of adjacent molecules. The variation of stiffness with temperature in the region below the melting point of the crystallites depends very much on the motions exhibited by the molecular segments in the non-crystalline regions.

Three separate molecular processes can be identified in phenyl/naphthyl liquid crystal polyesters using dynamic mechanical analysis (DMA). An example of a  $\tan \delta$  loss spectrum is shown in Figure 1 for polymers of the composition:



The upper  $\alpha$ -process at about 110°C appears to have many of the characteristics of the  $T_g$  transition of a conventional polymer and, as such can be associated with the onset of cooperative motions along the chain. The two lower processes appear to be associated with specific localized motions. By examining a series of polymers of different compositions Yoon and Jaffe<sup>2</sup> demonstrated that the prominent  $\beta$ -process in the region of 50°C is associated with the naphthyl moieties. They attributed the shallow  $\gamma$ -process at about -40°C to the onset of similar motions in the phenyl units.

The objective of the work described in this paper is to further clarify the nature of the  $\beta$ -process and in particular to discover the relationship of the naphthylene ring with the neighbouring ester links during the molecular motions. A study was made of the following three closely related polymers which contain the same proportions of naphthalene and phenyl units.



In each of these polymers the bordering ester linkages are joined in different ways to the 2-6 naphthalene rings. Both the mechanical and dielectric loss processes of these polymers were examined. A comparison of this data enables us to deduce how the motions of the ester sequences are linked with those of the naphthalene rings.

## EXPERIMENTAL

### Materials

The polyesters were synthesized using the methods described in the patent literature<sup>3</sup>. The polymers were compression moulded into sheets of thickness 1.5 mm. The polymers were held in the melt state in the press for 2 min to allow some degree of macroscopic randomization before cooling in the press to room temperature. The sheets were then post annealed at 250°C for 30 min to enable crystalline order to develop and to establish a level of crystallinity that would not change significantly during the subsequent dielectric and mechanical measurements.

### Dielectric loss

The dielectric measurements were made using disc specimens, approximately 53 mm diameter, cut from the

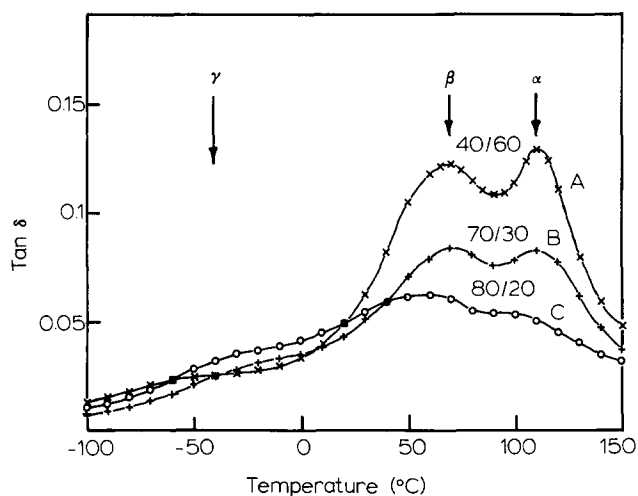


Figure 1 Tan  $\delta$  loss from dynamic mechanical analyses of copolymers of the form

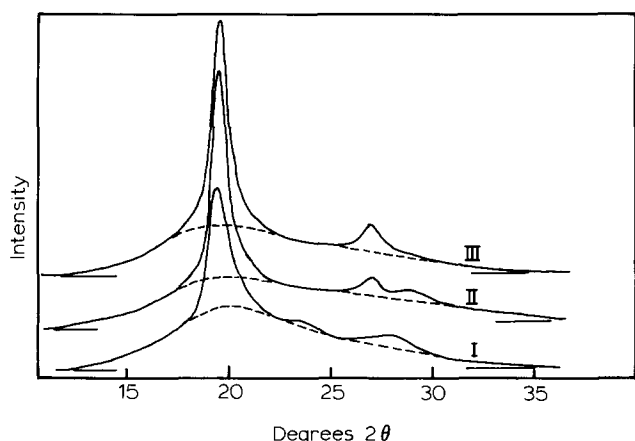
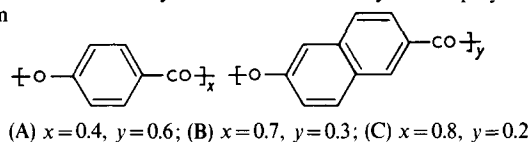


Figure 2 WAXS diffractograms from copolymers I, II and III

1.5 mm thick sheets. Intimate electrodes of evaporated gold were used. The specimens were mounted in a fully screened three terminal sample holder in an air circulating oven. The measurements were made at a series of fixed temperatures using a General Radio Capacitance Measuring Assembly type 1620A. Because of the time needed to equilibrate at each temperature point, data over the whole range  $-40^{\circ}$ – $220^{\circ}\text{C}$  could only be obtained by making overnight breaks in the measurement. This resulted in mismatching of points recorded at the same temperature on a subsequent day. These discontinuities in data are attributed to small changes in the molecular arrangements during the overnight intervals between recording.

**Dynamic mechanical analysis**

Rectangles of 25 mm  $\times$  10 mm were cut from the same moulded sheets. These were examined with a Du Pont 981 DMA with a cryogenic attachment. The mechanical loss spectrum was obtained from  $-140^{\circ}\text{C}$  to  $250^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C min}^{-1}$ .

**WAXS**

The wide-angle X-ray scattering from the sheets were measured using a Philips 1050 goniometer in the trans-

mission mode with the sheets mounted perpendicular to the incident radiation (CuK $\alpha$ ).

**RESULTS**

The WAXS diffractograms obtained from the three polymers are shown in Figure 2. All show a dominant diffraction peak at  $2\theta \approx 19.5^{\circ}$ , together with other smaller peaks superimposed on a broad, amorphous halo. Previous work has shown that such sharp peaks can be associated with relatively small and imperfectly ordered crystalline regions. By drawing in the amorphous backgrounds as indicated in Figure 2 and measuring the relative area of the sharp peaks and the halo, we deduce that the weight fraction of the polymers associated with the crystallites is about 35% in all three cases. We can therefore summarise that the remaining 65% is available to contribute to the loss processes as detected by DMA and dielectric loss measurements.

The tan  $\delta$  loss derived from the DMA is shown in Figure 3. In all cases the three main processes can be discerned, although there are differences in the details. The  $\alpha$ -processes are at about  $110^{\circ}\text{C}$ . There are prominent  $\beta$  processes in the region around  $50^{\circ}\text{C}$  and smaller  $\gamma$ -processes at about  $-40^{\circ}\text{C}$ .

The dielectric loss factor as a function of temperature for polymer I is shown in Figure 4. In this case there is a

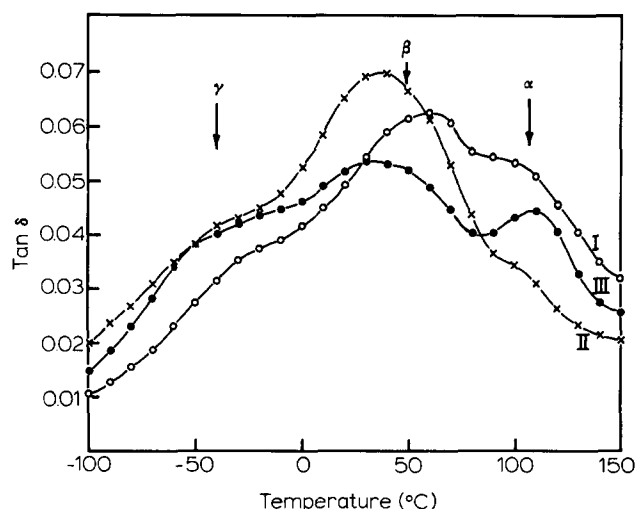


Figure 3 Tan  $\delta$  loss from dynamic mechanical analyses of copolymers I, II and III

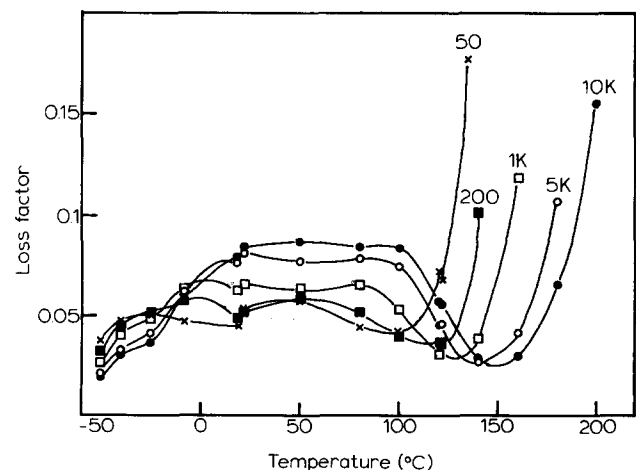


Figure 4 Dielectric loss  $\epsilon''$  of polymer I at frequencies 50, 200, 1000, 5000 and 10000 Hz

reasonable continuity in the data at the two overnight breaks in measurements at 20°C and 120°C. The profile of the loss factor is similar in character at each of the probing frequencies, the main difference being a shift along the temperature axis. For example at 1 kHz, there is a broad plateau spreading from -10°C to +80°C, with the hint of a shoulder at about -35°C. This plateau region appears to be a composite of more than one process. In fact at lower frequencies the plateau appears to separate into two distinct humps. At higher temperatures, the dielectric loss drops sharply and then suddenly climbs steeply. We associate this sharp rise to the onset of electrical conduction processes. It will be noted that at 50 Hz this increase occurs at about 130°C which according to Figure 3 would be close to the mechanical  $\alpha$ -process at this frequency. It is not uncommon to find electrical conduction effects after the onset of the cooperative main chain motions that are associated with a  $T_g$  transition.

Figure 5 is an attempt to construct a frequency versus temperature contour map from the data in Figure 4. From this presentation, the plateau region appears as a broad ridge which with reducing frequency gradually separates into two parallel spurs. Extrapolation of these spurs to a frequency of 20 Hz brings them very close to the positions of the  $\beta$  and  $\gamma$  processes detected by DMA in Figure 3.

It is therefore reasonable to assign these processes in the dielectric and mechanical loss to the same molecular origin.

The dielectric loss factor for polymers II and III are shown in Figures 6 and 7. In the case of polymer II, the

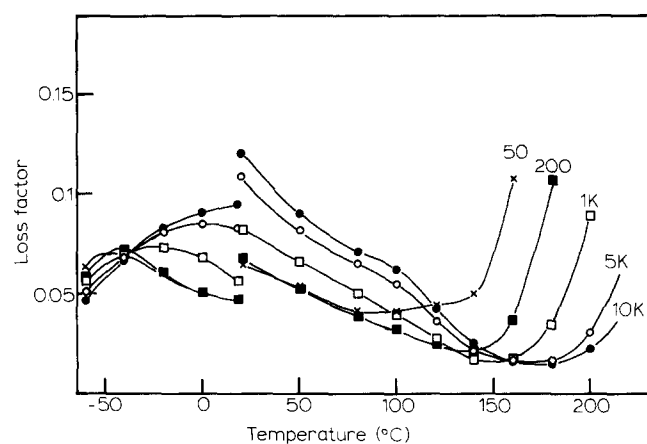


Figure 6 Dielectric loss  $\epsilon''$  of polymer II at frequencies 50, 200, 1000, 5000 and 10 000 Hz

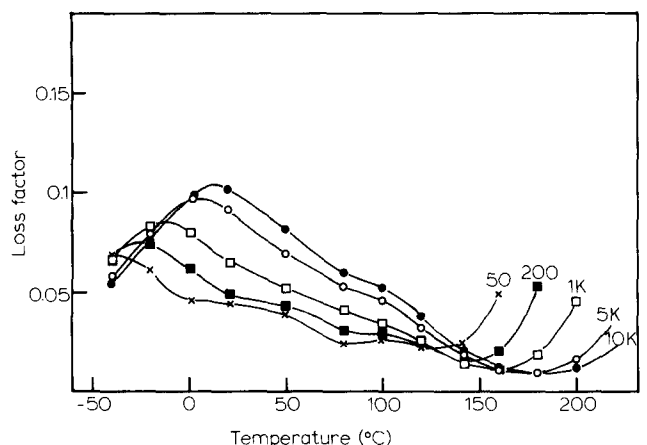


Figure 7 Dielectric loss  $\epsilon''$  of polymer III at frequencies 50, 200, 1000, 5000 and 10 000 Hz

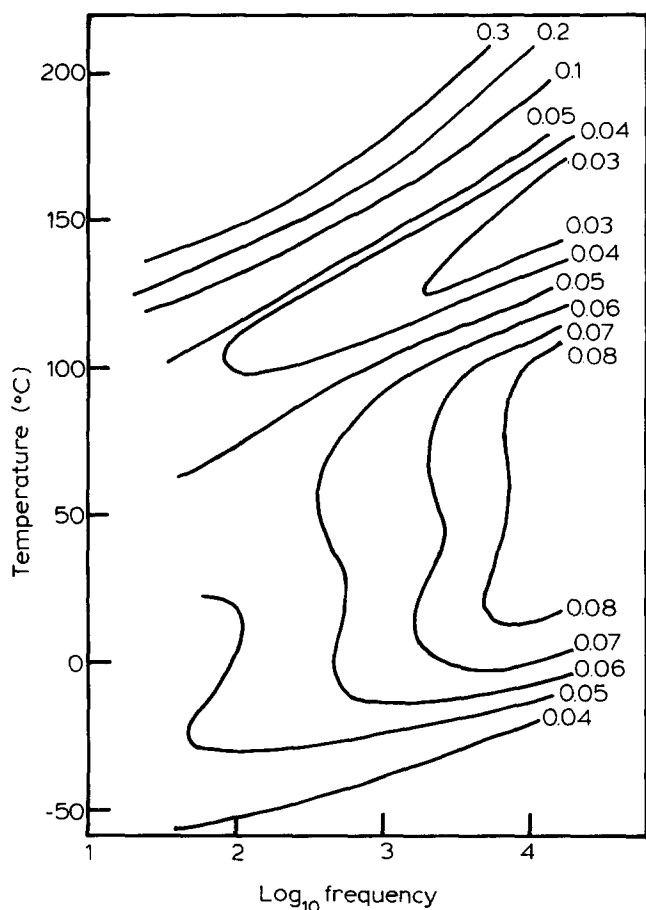


Figure 5 Contour map of dielectric loss of polymer I as a function of frequency and temperature

mismatch in the experimental data at the break at 20°C is rather poor. Despite this, there are strong similarities in the behaviour of these two polymers which is different in character to that of polymer I. Both show one sharper maximum in the loss at lower temperatures rather than the broad plateau. At the higher temperatures there is again a sudden rise in loss at about the region associated with the  $\alpha$ -process. The frequency-temperature contour maps shown in Figures 8 and 9 emphasize these features. There now appears to be a clear sharp ridge in the loss factor which on extrapolating to the 20 Hz region agrees well with the DMA  $\gamma$ -process. There is a complete absence of a clear dielectric loss process associated with the  $\beta$ -process in these two polymers.

## DISCUSSION

The most noteworthy observation to emerge from the dielectric study is the virtual absence of the  $\beta$  process in polymers II and III, whereas there is a very prominent contribution in the same region in polymer I. The DMA data shows that there are mechanical  $\beta$ -loss processes in all three polymers, so that the absence of a dielectric response appears to be directly attributable to local differences in the relationship of the naphthalene residue with the bounding ester groups.

In their study of the bond rotation energies of aromatic polyesters, Hummel and Flory<sup>4</sup> propose that least

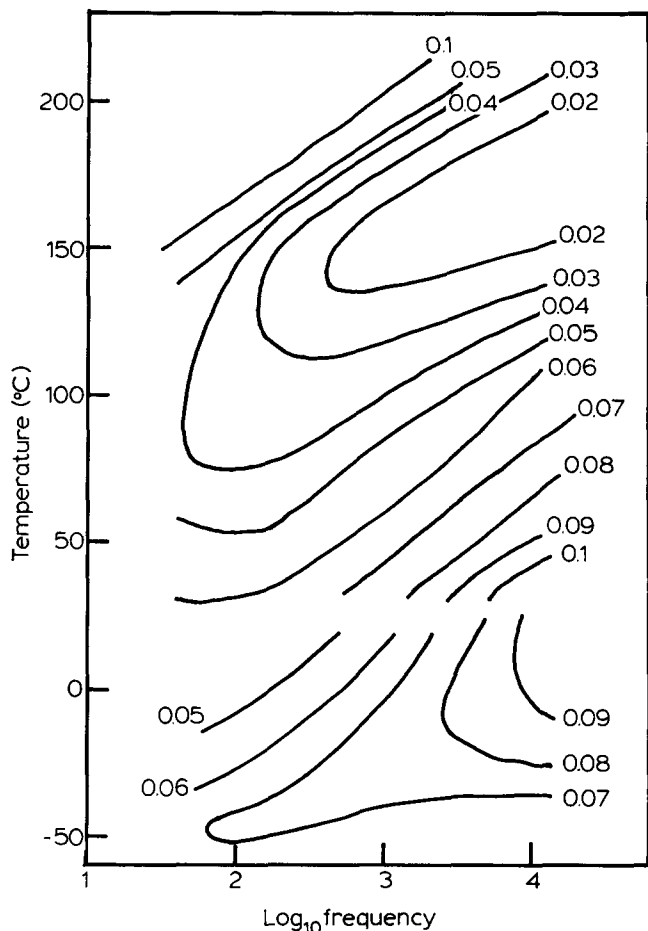


Figure 8 Contour map of dielectric loss of polymer II

resistance to rotation in the main chain is around the oxygen–aromatic link. They concluded that there are two minima at about  $\pm 55^\circ$  about the all planar position. The energy barrier to move past the perpendicular position was relatively low at  $0.25 \text{ kcal mol}^{-1}$ . Movement about the other ester links was very much more restrictive. These conclusions lead to the view that to a first approximation the carbonyl oxygens lie in the plane of the neighbouring phenyl ring, while most of the rotational motions of phenyl residues involve motions around the oxygen–phenyl bond. Although no corresponding calculations were performed on main chain naphthyl polyesters, there are no reasons for believing that similar principles will not apply in this case too.

As illustrated in Figure 10 the relationship of the naphthalene residue to the bounding ester links is different in each of the three polymers. Using the simplifying assumption that the naphthalene unit can only move by rotating about the two oxygen–aromatic links on each side, then one can see that in polymer I there will be one carbonyl group rigidly rotating with the naphthyl rings. In polymer II, there will be two neighbouring carbonyls moving in unison with the naphthyl group, whereas in polymer III, the naphthyl group will be moving as an isolated rigid unit. There are differences in the size of the rigidly rotating unit and in the degree of crankshaft motion of the nearest neighbours along the chain which could probably account for some of the differences in the dynamic mechanical spectrums resulting from such a motion.

In order that these same rotation motions can be excited by an applied electric field it is necessary for an

electric dipole to be associated with the rotating unit. This condition is clearly satisfied in polymer I by the permanent dipole associated with the carbonyl group. The converse situation occurs in polymer III where there are no permanent dipoles ‘rigidly’ associated with the naphthalene residue. This would account for the absence of a dielectric  $\beta$ -loss process. In polymer II there are two carbonyl dipoles associated with the naphthalene. The

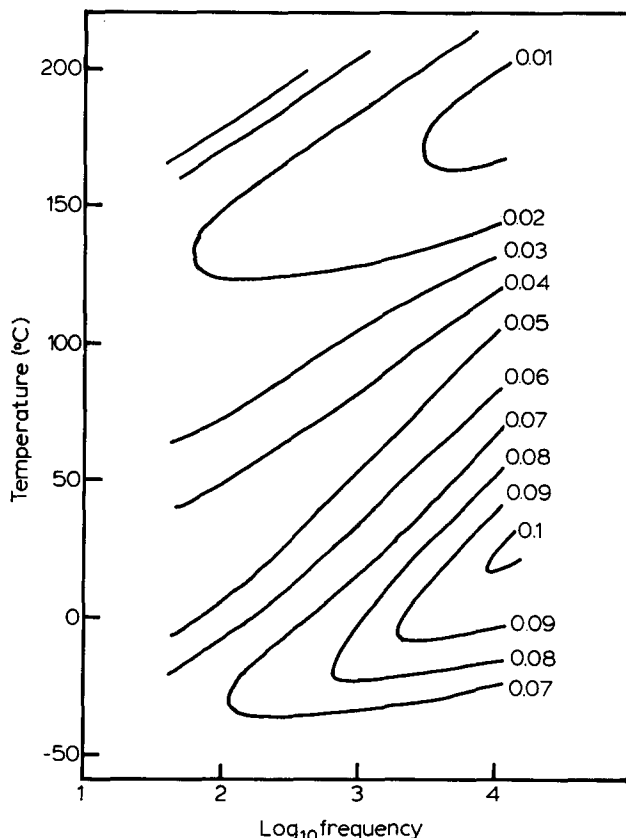


Figure 9 Contour map of dielectric loss of polymer III

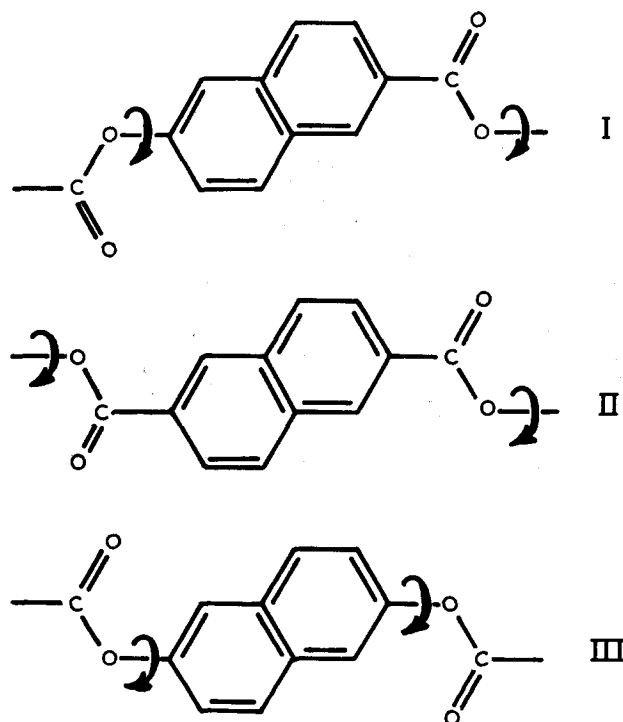


Figure 10 Scheme of rotation of naphthalene units

absence of a dielectric  $\beta$ -loss in this polymer could be accounted for if these two dipoles were in a symmetrical conformation (as in *Figure 10*) so that there was no net dipole associated with the naphthalene unit.

## CONCLUSIONS

The systematic absences of the dielectric loss relative to the mechanical loss process confirm that the  $\beta$  process is associated with the motion of the naphthalene rings. The naphthalene motions are strongly coordinated with any carbonyl group that is an immediate neighbour, such that the naphthalene group and the immediate neighbour carbonyls tend to move as a total entity. The motions appear to involve rotations around the nearest oxygen-naphthyl links which are aligned along the main chain

axis of the polymer. When the neighbouring oxygen-naphthyl links are not colinear, the rotations about the chain axis will be associated with a crankshaft movement.

## ACKNOWLEDGEMENTS

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