Dielectric relaxation of liquid crystalline main chain polyethers

U. W. Gedde*†, F. Liu, A. Hult†, A. Gustafsson†, H. Jonsson† and R. H. Boyd
Department of Materials Science and Engineering and Department of Chemical Engineering, University of Utah, Salt Lake City, Utah 84112, USA
(Received 18 December 1989; revised 9 March 1990; accepted 30 March 1990)

Dielectric permittivity and loss have been measured over the frequency range 10^{-3}–10^3 Hz between 100 K and 400 K for physical 50/50 (w/w) mixtures of dielectrically inactive linear polyethylene and liquid crystalline main chain polyethers based on bis(4-hydroxyphenoxy)-*p*-xylene and 4,4′-dihydroxy-biphenyl combined with methylene spacers of different lengths ranging from 2 to 12 carbons. There are two transitions in these polymers: α, the glass–rubber transition occurring at 295–307.5 K (10 Hz) for the polymers with spacer groups of 8–12 carbons and at 340 K (10 Hz) for the polymer (oligomer) with a spacer group of 2 carbons; and β, a sub-glass transition exhibiting Arrhenius behaviour with activation energies ranging from 49 to 54 kJ mol^{-1}. The relaxation strength of the β process increases with increasing content of aliphatic polar bromine/hydroxyl end groups.

(Keywords: liquid crystalline polymers; main chain polyethers; dielectric measurements; thermal analysis; relaxation)

INTRODUCTION

During the 1980s the dielectric relaxation of liquid crystalline main chain polyesters received attention and a few papers were published[1–6]. Completely aromatic, rigid main chain polymers based on naphthyl and phenyl esters display three relaxation processes[1–3]: an α process at about 110°C associated with the glass–rubber transition; a β process at 50°C associated with a co-ordinated rotation of the naphthalene groups about the main polymer axis; and a γ process at −40°C associated with rotation of the phenyl groups. The latter two relaxation processes exhibit an Arrhenius temperature dependence with activation energies of 105 (β) and 50 (γ) kJ mol^{-1}, respectively[3].

Semi-rigid main chain polymers follow a somewhat different scheme. Wendorff *et al.*[4] observed two dielectric relaxation processes in main chain polyesters with methylene spacers (6 and 10 carbon atoms); a glass–rubber transition (α) at about 100°C and a sub-glass process (β) at −40°C with an activation energy of 50–70 kJ mol^{-1}. Gedde *et al.*[5] showed that nematic poly(*p*-hydroxybenzoic acid-*co*-ethylene terephthalate) [P(HBA-ETP)] displays three transitions: α_{HBA}, the glass–rubber transition of the HBA-rich phase, α_{ETP}, the glass–rubber transition of the ETP-rich phase and β, a sub-glass transition assigned to both the HBA- and ETP-rich phases. The symmetrically broadened β process showed a close resemblance to the β process in PETP with regard to activation energy (56 kJ mol^{-1}) and width. The α_{ETP} transition occurred at lower temperatures than in PETP and had a width similar to that associated with semicrystalline PETP. The 0.6–0.4 P(HBA-ETP) copolymer displayed a double α_{ETP}, which may indicate the presence of two different ETP-rich phases in this polymer. The molecular origin of the β process has not yet been elucidated. It may be due to localized motions of the methylene spacer group or it may be associated with rotation of phenyl groups.

This paper presents data from dielectric measurements and thermal analysis of main chain polyethers based on both bis(4-hydroxyphenoxy)-*p*-xylene and 4,4′-dihydroxy-biphenyl combined with methylene spacers of different lengths ranging from 2 to 12 carbons. The polyethers based on bis(4-hydroxyphenoxy)-*p*-xylene belong to a new class of liquid crystalline polymers in which the rigid link in the mesogen is replaced by a more flexible group[7]. Percec and Yourd[8] have introduced the term 'flexible rod like' for this type of mesogen.

EXPERIMENTAL

Liquid crystalline polyethers based on bis(4-hydroxyphenoxy)-*p*-xylene and three different methylene spacers having 2, 11 and 12 carbons, respectively (HPX-C2, HPX-C11 and HPX-C12) and on 4,4′-dihydroxy-biphenyl combined with two spacer units (8 and 10 carbons) (BP-8/10) were prepared by a phase-transfer-catalysed Williamson ether synthesis. Details of the preparation of these polymers and their phase transitions and morphologies are presented in references 7, 9 and 10. The structures of the polymers (oligomer in case of HPX-C2) are shown in *Figure 1*.

The number average molecular masses determined by end-group analysis were: $M_n = 720$ (dimer, HPX-C2), 10 300 (HPX-C11), 7600 (HPX-C12) and 3100 (BP-8/10). HPX-C2 is an oligomer (dimer) which is almost exclusively terminated by hydroxyl end groups and may exist in either of the two possible structures shown in *Figure 1*. The low molecular weight of HPX-C2 is due to the low solubility of the dimer in the organic phase and, as

---

* To whom correspondence should be addressed at: Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

† Present address: Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

0032-3861/91/071219-04

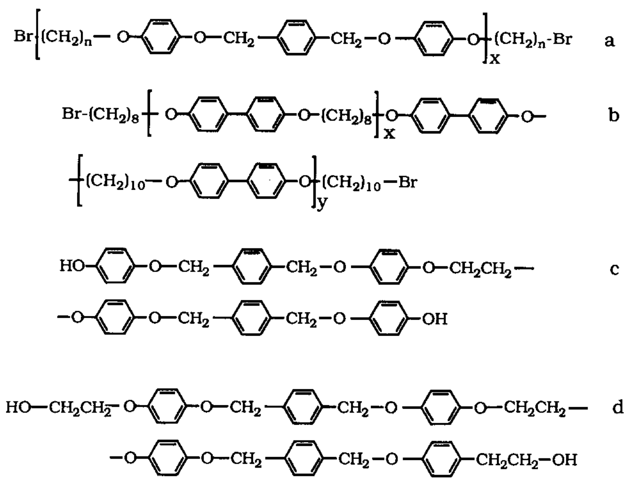

Figure 1 Chain structure of polymers and oligomers studied. (a) HPX-C11 ($n = 11$) and HPX-C12 ($n = 12$); (b) BP-8/10, statistical sequence of C8 and C10 spacer groups; (c) HPX-C2, dimer with phenolic hydroxyl end groups; (d) HPX-C2, dimer with aliphatic hydroxyl end groups

pointed out by Percec *et al.*[11], due to the lack of anchomeric assistance in the oxonium transition state. The low solubility of the oligomer in the organic phase is the cause of the formation of hydroxyl end groups in HPX-C2. Phenolic hydroxyl end groups (*Figure 1c*) are produced by the precipitation of bis(4-hydroxyphenoxy)-*p*-xylene terminated oligomer. Aliphatic hydroxyl end groups (*Figure 1d*) are formed when an oligomer having bromoalkoxy chain ends enters the organic phase. The concentration of the phenoxy anions is very low in the organic phase mainly due to its low solubility. The hydroxyl ion will therefore compete with the phenoxy anion in the displacement of the bromine group, thus giving aliphatic alcohol chain ends[12]. The content of aliphatic alcohol chain ends in HPX-C2 has not been determined separately but is most probably significant.

Thermal transitions were revealed by heating the 5 mg samples at $10\ \mathrm{K\ min^{-1}}$ from 250 to 350 K in a Perkin-Elmer DSC-7 which was temperature- and energy-calibrated according to standard procedures. The dielectric work was carried out on 50/50 (w/w) blend samples of the polyethers and linear polyethylene (LPE). The presence of LPE made it possible to produce samples of sufficient mechanical strength. It was verified by dielectric measurements that the LPE component showed no measurable dielectric loss in the temperature and frequency range used. The samples (200 μm thick) were coated with gold–palladium in a vacuum sputterer. The dielectric apparatus was an IMASS TDS time domain spectrometer equipped with a Hewlett Packard series 300 computer. The time domain spectrometer is based on a design by Mopsik[13]. At time $t = 0$ a step voltage of 10 V was applied. This induced a charge, $Q(t)$, to flow through the sample and the complex capacitance as a function of frequency was obtained by a numerical Laplace transform, based on a cubic spline, of the time domain capacitance data. The latter covered a time period of 5 min and frequency domain data were obtained from 10^{-3}–10^{3} Hz. All measurements were carried out by first cooling the sample to 100 K and then heating it while making measurements at progressively higher temperatures. Temperature equilibrium was established prior to the actual measurements.

RESULTS AND DISCUSSION

All samples studied displayed two relatively weak dielectric relaxation processes, referred to respectively as α and β in order of descending temperature. A typical example (HPX-C12) is shown in *Figure 2*. The other samples exhibit similar dielectric relaxation behaviour, different only in the temperatures and strengths of the two relaxation processes (*Table 1*).

The α process appears most clearly at the higher frequencies whereas at the lower frequencies it is hidden by the rapid increase in both dielectric permittivity and

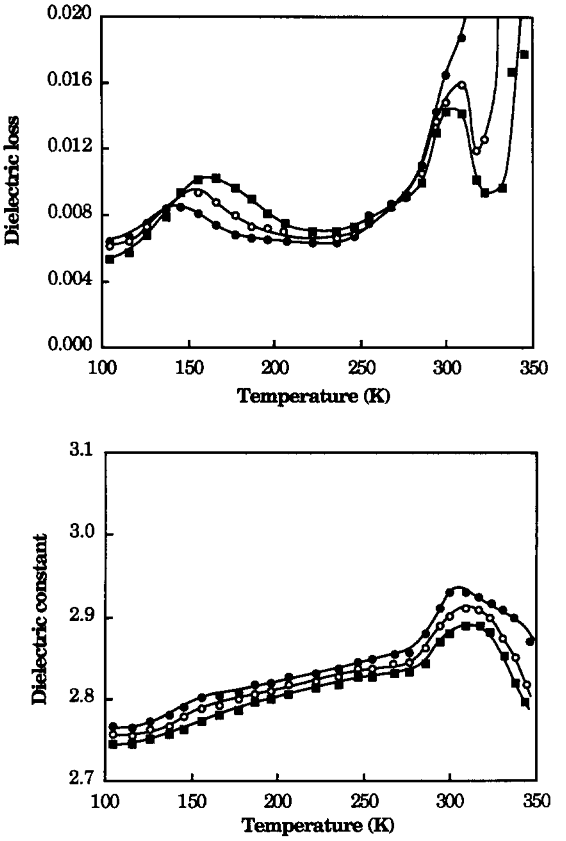

Figure 2 Dielectric loss and permittivity of HPX-C12/LPE (50/50 blend) at (●) 1, (○) 10 and (■) 100 Hz plotted *versus* temperature

Table 1 Summary of data for α and β relaxation processes

	HPX-C2	HPX-C11	HPX-C12	BP-8/10
$\varepsilon_r - \varepsilon_u$[a] ($\beta$)	0.44	0.16	0.14	0.26
ΔE[b] (β)	54.4	51.5	49.2	52.7
T_g (K)[c]	–	292	297	299
ΔC_p ($\mathrm{J\ g^{-1}\ K^{-1}}$)[c]	–	0.07	0.16	0.11
$\varepsilon_r - \varepsilon_u$[a] ($\alpha$)	0.14	0.25	0.20	0.20
T_{max} (K)[d] (α)	340	295	302	307.5
ΔH_{in} ($\mathrm{kJ\ kg^{-1}}$)[e]	168	69	117	109

[a] Estimated from isochronal dielectric permittivity *versus* temperature plots (10 Hz). The reported value was obtained by doubling the value obtained from the measurements of the 50/50 blends
[b] Activation energy in $\mathrm{kJ\ mol^{-1}}$
[c] By d.s.c. as the mid-point of the glass transition
[d] Temperature for maximum dielectric loss at 10 Hz
[e] Total endothermal heat in all first-order transitions from the isotropic state down to room temperature

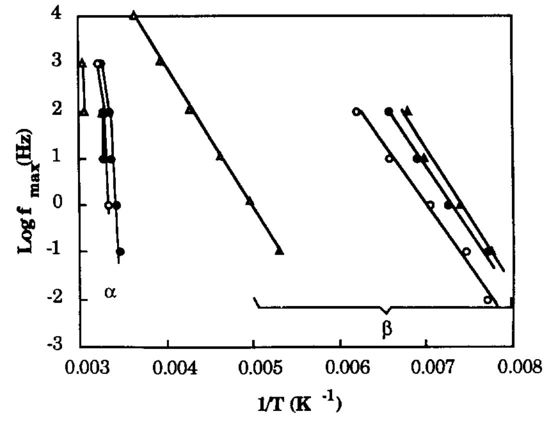

Figure 3 Temperature dependence of α and β relaxations for all the polymers studied. The data are obtained from plots of isochronal data of dielectric loss *versus* temperature. (△) HPX-C2, (●) HPX-C11, (○) HPX-C12 and (▲) BP-8/10

loss due to the Maxwell–Wagner effect. The β process on the other hand is easily revealed in the whole frequency range.

Figure 3 shows the temperature dependence of the central relaxation time (τ) as obtained from isochronal dielectric loss *versus* temperature plots. The Arrhenius plots presented in *Figure 3* are constructed on the basis of the frequency (reciprocal relaxation time) and the temperature at the maximum of the dielectric loss *versus* temperature plots. The non-linear behaviour of the α process is typical for glass transitions whereas the rectilinear curves for the β process of the different samples are indicative of a typical sub-glass process. As shown in *Table 1*, the latter follows the Arrhenius equation ($\tau = \tau_0 \exp^{+\Delta E/RT}$) with an activation energy (ΔE) between 49.2 kJ mol^{-1} and 54.4 kJ mol^{-1}. The latter value obtained for HPX-C2 is very close indeed to that obtained for the corresponding aromatic polyester (PETP)[14]. The activation energy increases slightly with decreasing length of the spacer unit: ΔE is about 10% greater for HPX-C2 than for HPX-C12.

The temperature-independent relaxation time (τ_0) is also affected by the spacer length. *Figure 4* shows that data for the liquid crystalline main chain polyethers are in agreement with the data by Farrow *et al.*[15] for semicrystalline poly(methylene terephthalate) polymers.

The relaxation strengths ($\varepsilon_r - \varepsilon_u$, where ε_r is the relaxed and ε_u is the unrelaxed dielectric permittivity) are ideally obtained from Argand plots. Due to the weakness and broadness of the β process this was not possible for the present polymers. The relaxation strength can be estimated from isochronal dielectric permittivity *versus* temperature scans. This was done for the 10 Hz data by recording the difference in dielectric permittivity between the high (β: at 210 K for HPX-C11, HPX-C12 and BP-8/10; and at 280 K for HPX-C2) and low temperature (β: at 110 K for HPX-C11, HPX-C12 and BP-8/10; and at 125 K for HPX-C2) sides of the transition. The relaxation strength values presented were obtained by doubling the values obtained from the measurements of the 50/50 blends. *Table 1* shows that the relaxation strength of the β process is three times greater for HPX-C2 than for HPX-C11 and HPX-C12. The relaxation strength is thus an integrated measure of both the number of dipoles which participate and the extent of motion for the dipoles involved in the relaxation process.

Based on the high total endothermal heat, ΔH_{in}, value recorded for HPX-C2 (*Table 1*) it may be stated that the crystallinity of this material is not less than that of the other two polymers, and the difference in relaxation strength must therefore be due to other factors. *Figure 5* shows that there is a correlation between the relaxation strength and the overall content of polar bromine and hydroxyl end groups. It is worth noting that the dipole moment is about the same for the two end groups: 5.7×10^{-30} Cm for C–OH in C_2H_5OH and 6.3×10^{-30} Cm in C–Br in C_2H_5Br[16]. It may thus be postulated that the dielectric β relaxation to some extent is associated with the local main chain motions of the methylene spacer group adjacent to the polar end groups. Linear extrapolation of the trend from the data points of the three polymers (HPX-C11, HPX-C12 and BP-8/10) indicates however that the dielectric β process is not exclusively associated with the polar end groups. The relaxation strength (β) in the oligomeric sample (HPX-C2) is considerably lower than the value obtained by a linear extrapolation of the data for the polymers (*Figure 5*). This may be due to only a portion of the hydroxyl end groups in HPX-C2 being aliphatic, the other part being linked directly to a phenyl group (*Figure 1*).

The α process exhibits all the features typical of glass transitions. The temperature dependence deviates from

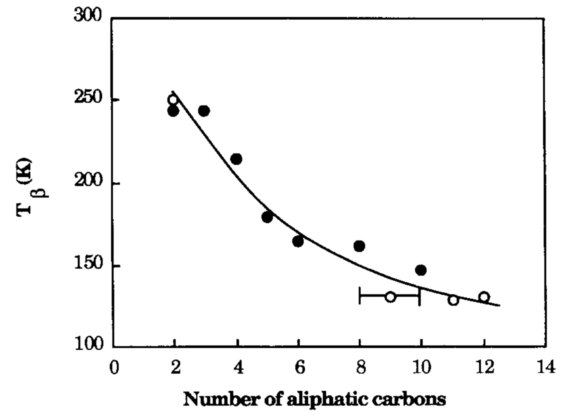

Figure 4 Temperature for maximum in dielectric loss at 100 Hz plotted *versus* number of carbons in the aliphatic group. Data for poly(methylene terephthalate) (●) according to Farrow *et al.*[15] are presented together with the data for the main chain polyethers (○) of this study

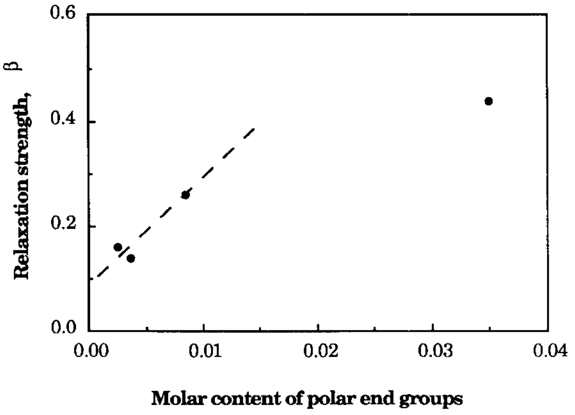

Figure 5 Relaxation strength ($\varepsilon_r - \varepsilon_u$) of the β process plotted *versus* the molar fraction of polar end groups [bromine (HPX-C11, HPX-C12 and BP-8/10) or hydroxyl (HPX-C2)]

the simple Arrhenius equation (*Figure 3*). This is further substantiated by differential scanning calorimetry (d.s.c.) data revealing a stepwise increase in specific heat (ΔC_p) at the corresponding temperatures (*Table 1*). The observed decrease in the glass transition temperature, T_g (T_{max}), with increasing length of the spacer group is expected (*Table 1*). It is worth noting that T_g (T_{max}) is lower for HPX-11 than for HPX-C12 (*Table 1*) in contradiction to the aforementioned general trend. The crystallinity is however higher in HPX-C12 than in HPX-C11[7] which is also reflected in the significantly higher ΔH_{in} value obtained for HPX-C12 (*Table 1*). The non-crystalline component of HPX-C12 should thus be more constrained and lead to a higher T_g. HPX-C2 displayed a dielectric α process with a relaxation strength of about 50–70% of the relaxation strength of the other polymers, but no glass transition was revealed by d.s.c. (*Table 1*). The relaxation strength values were obtained by doubling the difference in dielectric permittivity (10 Hz) between the high temperature and low temperature side of the transition. This apparently contradictory finding may be explained by the higher overall content of polar end groups in this polymer in combination with the high degree of crystallinity in this material (see ΔH_{in} value shown in *Table 1*). Thus, dielectric registration of the α process in HPX-C2 is more sensitive than calorimetric registration.

ACKNOWLEDGEMENTS

The reported studies have been sponsored by The National Swedish Board for Technical Development (STU) grant 86-03476P, by The Swedish Natural Science Research Council (NFR) grants K-KU 1910-300 and RA-A 1910-104, and by the National Science Foundation (USA).

REFERENCES

1 Blundell, D. J. and Buckingham, K. A. *Polymer* 1985, **26**, 1623

2 Yoon, H. N. and Jaffe, M. *Am. Chem. Soc., Div. Polym. Chem., Polym. Prepr.* 1983, **24**, 127

3 Alhaj-Mohammed, M. H., Davies, G. R., Abdul Jawad, S. and Ward, I. M. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 1751

4 Wendorff, J. H., Frick, G. and Zimmermann, H. *Mol. Cryst. Liq. Cryst.* 1988, **157**, 455

5 Gedde, U. W., Buerger, D. and Boyd, R. H. *Macromolecules* 1987, **20**, 988

6 Takase, Y., Mitchell, G. R. and Odayima, A. *Polym. Commun.* 1986, **27**, 76

7 Jonsson, H., Gedde, U. W., Werner, P.-E. and Hult, A. *Macromolecules* 1989, **22**, 1683

8 Percec, V. and Yourd, R. *Macromolecules* 1988, **21**, 3379

9 Shaffer, T. D. and Percec, V. *J. Polym. Sci., Polym. Lett. Edn* 1985, **23**, 185

10 Jonsson, H., Wallgren, E., Hult, A. and Gedde, U. W. *Macromolecules* 1990, **23**, 1041

11 Percec, V., Shaffer, T. D. and Nava, H. *J. Polym. Sci., Polym. Lett. Edn* 1984, **22**, 637

12 Shaffer, T. D., Jamaludin, M. and Percec, V. *J. Polym. Sci., Polym. Chem. Edn* 1985, **23**, 2913

13 Mopsik, F. I. *Rev. Sci. Instrum.* 1984, **55**, 79

14 Coburn, J. and Boyd, R. H. *Macromolecules* 1986, **19**, 2238

15 Farrow, G., Mcintosh, J. and Ward, I. M. *Makromol. Chem.* 1960, **38**, 147

16 Smyth, C. P. in 'Physical Methods of Organic Chemistry' (Ed. A. Weissberger), Vol. 1, 2nd Edn, Interscience, New York, 1949