Liquid Crystal Polymers

Thermotropic Polyesters with Mesogenic Groups Based on Substituted Hydroquinone Units and Highly Flexible Siloxan Spacer in the Main Chain

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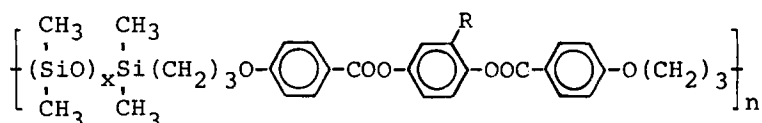
SUMMARY

New thermotropic Polyesters having mesogenic groups based on substituted hydroquinone units and highly flexible oligosiloxan spacer in the main chain, are synthesized and characterized. The mesophase formed at low temperature are studied by differential scanning calorimetry (DSC) and polarized light microscopy. The liquid crystalline behaviour of these polyesters, particulary their transition temperatures and the mesophase width could be explained on the basis of their structural features.

INTRODUCTION

In recent years there has been increased interest in liquid crystal polymers, especially after the development of high modulus fibres (Harrnell 1970; Morgan 1977). High tensile strength fibres can be prepared by spinning out of the lyotropic phase of some aromatic polyamide (Kwolek 1972; Kwolek et. al. 1977). Melt processed fibres can be prepared from polyesters. The basic structures in liquid crystal polyesters are benzene rings attached at para position through ester groups. They are derived from terephthalic acid plus hydroquinone or from p-hydroxybenzoic acid (Schaefgen et al. 1975; Jackson et al. 1980), although the melting temperatures are still too high for a normal spinning process without thermal degradation (Jackson 1980). To overcome these disadvantaqe p-hydroxybenzoic acid modified poly(ethylene terephthalate) was prepared, showing a decrease in the transition termperatures caused by the short aliphatic segments between the mesogenic units (Jackson et al. 1976; Jackson 1980). Later investigation showed that the polymers having rigid mesogenic units interconected through flexible oligomethylene spacer along the main chain enables the formation of thermotropic liquid crystalline phases (Roviello et al. 1975; Strzelecki et al. 1980; Van Luyen et al. 1980; Jin et al. 1980; Ober et al. 1982). Thermotropic Polyesters, containing mesogenic groups in the main chain separated by siloxan spacer (Aquilera et al. 1980; Jo et al. 1982) are of considerable interest because their phase transition temperatures are considerably

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lower than those in wich the mesogene group are bound through a oligomethylene spacer. We previously reported the synthesis and properties of several new series of polyesters with oligosiloxan spacer having thermotropic liquid crystalline properties. As expected the flexible dimethylsiloxan spacer has a remarkable influence on the glass transition; a drastical decrease down to -111°C is achieved by increasing the spacer length (Aguilera et al. 1983). It has been demonstrated by a number of investigators that the introduction of a lateral substitution along the rigid backbone (mesogenic units) as well reduces the melting and clearing temperature of the thermotropic polymeres (Jin et al. 1980; Majnusz et al. 1983). To attain a better understanding of the effect of the flexible oligosiloxan spacers and mesogenic groups on the thermotropic properties of this polyester, and also as an contribution to develop polymers with low glass transition, we have synthesized and characterized polyester with substituted hydroquinone and highly flexible spacer, as follow:

$$\left[\begin{array}{c} CH_3 \quad CH_3 \\ | \qquad | \\ (SiO)_x Si(CH_2)_3 O\text{-}\bigcirc\text{-}COO\text{-}\bigcirc^R\text{-}OOC\text{-}\bigcirc\text{-}O(CH_2)_3 \\ | \qquad | \\ CH_3 \quad CH_3 \end{array} \right]_n$$

x : 2,3,4,5

R : CH_3 , OCH_3 , Cl

RESULTS AND DISCUSSION

The thermotropic polyesters contain 2-substituted hydroquinone and oligosiloxane spacers were synthesized by addition of the α,ω-allyloxymesogenic units (Aguilera 1984) to α-dimethylsilanyl-ω-hydrogenooligodimethylsiloxane (Patnode et al. 1946; Greber et al. 1960) catalized by hexacloroplatinic acid.
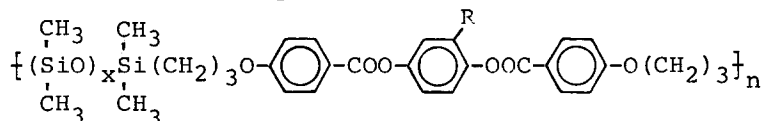
The phase behaviour of this polyesters 1-3 are presented in table, the data for the polyesters 4a – 4d were taken from our previous work (Aguilera et al. 1983) and are included in the table for comparation.

Each of the polymers forms thermotropic liquid crystal phase even at room temperature. All the polyesters do not crystalline, their liquid crystalline state is frozen in bellow the glass transition temperature.

The DSC thermograms for each polymer with substituted hydroquinone contend well separated phase transition assignable to the glass transition, g, and clearing point, i, of the polyester. The endothermic peak corresponding to the isotropic transition of these polyesters were much sharper than those polyesters with unsubstituted hydroquinone (e.g. Fig. 1). The clearing point for these thermograms were verifed by visual observation of the optical changes for the polymer on a hotstange of a polarising microscope.

As expected the substitution on the hydroquinone units for these polyesters have a remarcable influence on the phase width and on the clearing temperature to compared with those without substitution (Tab. 4a-4d). Substituents on hydroquinone units

TABLE : Phase transition of liquid crystalline Polyesters with substituted hydroquinones.

$$\left.\begin{array}{cc} CH_3 & CH_3 \\ | & | \\ (SiO)_x Si(CH_2)_3 \\ | & | \\ CH_3 & CH_3 \end{array} O-\bigcirc-COO-\bigcirc\!\!\!\!^{R}-OOC-\bigcirc-O(CH_2)_3\right\}_n$$

Polymer	x	R	Phase transitions[a] temperature in °C						Phase width
1a	2		g	3	lc	37	lc	60 i	57
b	3	CH$_3$	g	-13	lc			45 i	58
c	4		g	-22	lc			41 i	63
d	5		g	-28	lc			32 i	60
2a	2	OCH$_3$	g	26	lc			66 i	40
b	3		g[b)		lc			35 i	-
3a	2		g	-31	lc	24	lc	78 i	81
b	3	Cl	g	- 8	lc			75 i	83
c	4		g	-20	lc			37 i	57
d	5		g	-30	lc			31 i	61
4a	2		k	35	s			130 i	95
b	3	H	g	5	s			114 i	109
c	4		g	-13	lc			94 i	107
d	5		g[b)		lc			87 i	-

a) g : glassy, lc : liquid crystalline, k : crystalline, i : isotropic
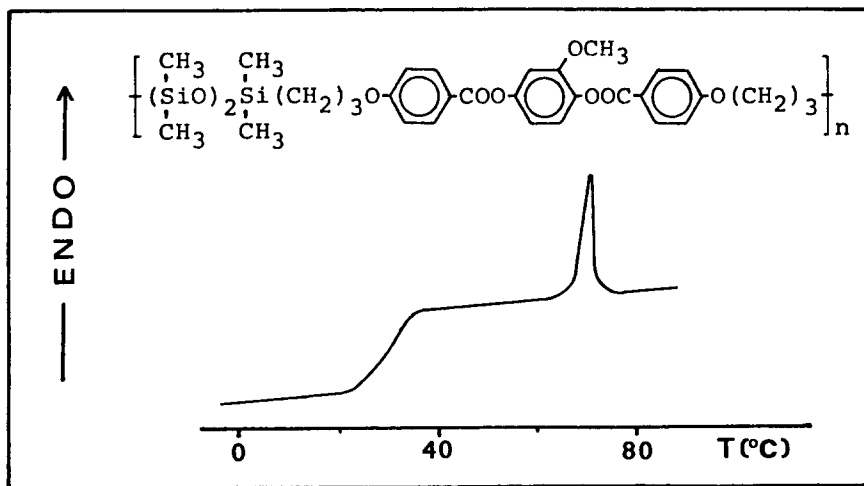b) could not be determined by DSC.

Fig. 1. DSC heating curve of liquid crystal polyester 2a.

destabilised the mesophase of polymers lowered their clearing temperature. The change from ring-H to a ring-R bond will increase the molecular polarizability and possible also the molecular polarity of the mesogenic units, they would be expected to enhance of the intermolecular attractions and increase the glass transition and clearing point. However, the predominant steric effect of the substituents to cause destabilisation of the liquid crystalline phase. Similar trend has been observed for many organic compound of low molecular weight, which were known to be thermotropic (Young et al. 1972; Gray et al. 1974).

The values for the glass transition of these polyesters were found to be low temperature, that those polyesters containing hydroquinone units without lateral substituents and similar spacer length (Tab.). By increasing the spacer length decrease the glass-and clearing transition. The phase behaviour of the polyester is shown in Fig. 2 for the polyester 1a-1d demonstrating that the phase width is near retained with increasing spacer length up to 5 siloxane units.
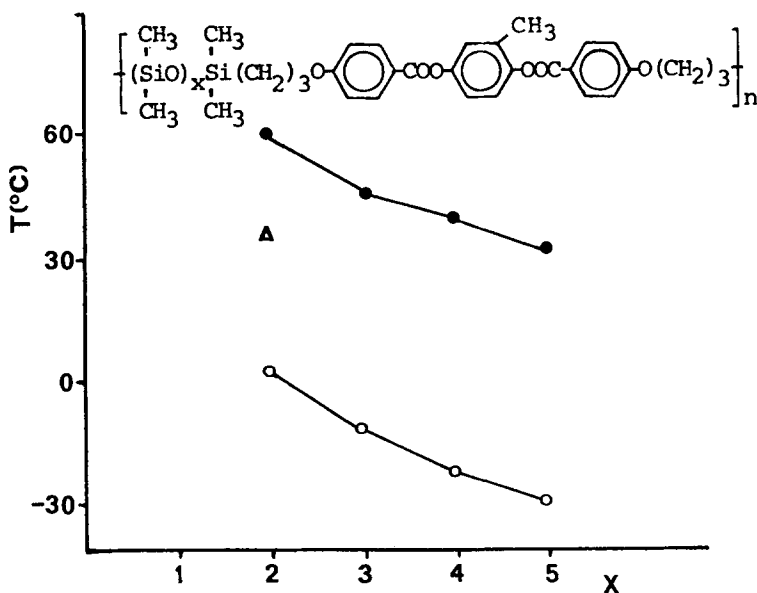

Fig. 2. Influence of the length of the siloxane spacer on the transition temperatures of the liquid crystalline polyester 1a-1e (•): clearing point; (Δ): phase transition point; (o): glass transition temperature; (x): number of siloxane units.

Another interesting observation was that by short siloxan units, x:2,3 the polyesters containing cloro substituted hydroquinone (see Tab. 3a-3b) have greater phase width that those polyesters with methyl substituent, by longer spacer length, those effects dissapear.

The unspecific texture of the lateral substituted polyester makes impossible to relate unequivocally the mesophase by pola-

rizing microscopy. Additional studies are in progress on this point.

EXPERIMENTAL PART

α,ω-allyloxymesogenic units.

Bis(4-allyloxybenzoic acid) ester, derivatives of 2-substituted hydroquinone was prepared as previously reported (Aguilera 1984).

Polyesters.

All of the polyesters were prepared from equimolar mixtures of α,ω-allyloxymesogenic units and α-dimethylsilanyl-ω-hydrogeno-oligodimethylsiloxane in the presence of Wacker Oil[c) catalyst based on H_2PtCl_6. The components were dissolved in a minimumm amount of dry THF and the reaction solution was stirred in a nitrogen atmosphere at 60°C. After complete addition (18-20 h, dissappearance of the Si-H-absorption at 2140 cm^{-1}), most of the THF is evaporated. The polyester is precipitated from methanol. Further purification is achieved by gel permeation chromatography (eluent: dry THF, column material: PVA 2000 from Merck; or Bio Bead s-x3 2000, from Bio Rad Laboratories).
    The molecular weight of the polyesters were determined by vapour pressure osmometry (Knauer) in toluen. Typical results from M_n are: 5400 (1d), 6400 (2a).
    The Polyesters give correct IR, ^{1}H-NMR and elemental analyses; transition temperatures were measured in a Perkin-Elmer DSC 2c and on polarizing microscope (Leitz Ortholux POL BK II equipped with a hotstange, Mettler's FP-5).

REFERENCES

AGUILERA C., RINGSDORF H., SCHNELLER A., ZENTEL R.: IUPAC MACRO, Florence, Preprints, 3, 306 (1980).
AGUILERA C., BARTULIN J., HISGEN B., RINGSDORF H.: Makromol. Chem. 184, 253 (1983).
AGUILERA C.: Acta Cient. Venezolana, (1984) in press.
GRAY G.W. & WINSOR P.A.: Liquid Crystal and Plastic Crystal Vol. 1, pp. 125-138 (1974).
GREBER G., METZINGER L.: Makromol. Chem. 39, 167 (1960).
HARRNELL J.W.: Polym. News 1(1), 8-13 (1970).
JACKSON W.J., MORRIS J.C.: US Pat. 4181972 (January 1, 1980).
JACKSON W.J.: Br. Polym. J. 12, 154 (1980).
JACKSON W.J., KUHFUSS H.F.: J. Polym. Sci. Polym. Chem. Ed. 14, 2043 (1976).
JIN J.I., ANTOUN S., OBER C., LENZ R.W.: Br. Polym. J. 12, 132 (1980).
JO B.W., JIN J.I., LENZ R.W.: Eur. Pol. J. 18, 233 (1982).
KWOLEK S.L.: US Pat. 3671542 (June 20, 1972).
KWOLEK S.L., MORGAN P.W., SCHAEFGEN J.R., HULRICH L.W.: Macro-molecules 10, 1390 (1977).

[c)] Wacker Chemie Burghausen FRG.

MAJNUSZ J., CATALA J.M., LENZ R.W.: Eur. Polym. J. 19, 1043, (1983).

MORGAN P.W.: Macromolecules 10, 1381 (1977).

OBER C., JIN J.I., LENZ R.W.: Polym. J. 14, 9, (1982).

PADTNODE W., WILCOCK D.F.: J. Am. Chem. Soc. 68, 358 (1946).

ROVIELLO A., SIRIGU A.: J. Polym. Sci., Polym. Lett. Ed. 13, 455 (1975).

SCHAEFGEN J.R., PLETCHEN T.C., KLEINSCHUSTER J.J.: Belg. Pat 828935 (1975).

STRZELECKI L., VAN LUYEN D.: Eur. Polym. J. 16, 299 (1980).

VAN LUYEN D., STRZELECKI L.: Polym. J. 16, 303 (1980).

YOUNG W.R., HALLER I., GREEN D.C.: J. Org. Chem. 37, 3707 (1972).