

Synthesis, Thermal, and Mechanical Characterization of Liquid-Crystalline Polyhydroxyethers

ALBERT BRUGGEMAN,^{1,2} SEBASTIAAN B. DAMMAN,^{1,*} ALOIS H. A. TINNEMANS¹

¹ TNO Institute of Industrial Technology, Division of Materials Technology, P.O. Box 6031, 2600 JA Delft, The Netherlands

² Eindhoven Polymer Laboratories, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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ABSTRACT: High molecular weight liquid-crystalline polyhydroxyethers, containing functional hydroxy groups, were synthesized from an aromatic diol and the diglycidylether of an aromatic diol. The polymers showed a liquid-crystalline melt when about 70% or more of the aromatic units in the chain were biphenyl units. Tensile modulus values varied from 3 GPa for as-cast films to 6 GPa for drawn films. These polymers are potentially suitable candidates to reinforce common thermoplastics by reactive blending. For this purpose polyhydroxyethers have been prepared, having a liquid-crystalline melt in the processing range of PET, viz. 260–290°C. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1971–1978, 1997

Key words: polyhydroxyethers; liquid-crystalline; film drawing; mechanical properties; reactive blending

INTRODUCTION

There has been an increasing scientific and industrial interest in thermotropic liquid-crystalline polymers (TLCPs) for use as a reinforcing component in thermoplastics. The main advantages of TLCP-thermoplastic blends are an *in situ* reinforcement during processing, a lowering of the melt viscosity, a lower wear of the processing equipment compared to glass-filled thermoplastics, and the possibility for recycling. The main problem to be solved in almost all fiber-reinforced polymers is the poor adhesion between fiber and matrix,¹ which is often the cause of failure. The adhesion might be improved by physical or chemical interactions between fiber and matrix. To in-

crease the adhesion by a chemical reaction at the interface, both the TLCP and the matrix polymer should contain functional groups that are capable of reacting with each other.

It is well known that linear high molecular weight polymers with functional groups can be made from bisphenol A and epichlorohydrin in two steps.^{2,3} These polyhydroxyethers have pendant hydroxyl groups and are named “phenoxy.” They are tough and ductile thermoplastics with a good impact resistance, good barrier properties, and a good compatibility with polar materials and surfaces. When blending these phenoxyes with PBT⁴ or liquid-crystalline polyesters,^{5,6} interchange reactions have been found to occur between the hydroxy and ester groups. In this study, the synthesis is described of analogous polymers with thermotropic liquid-crystalline behavior. To induce liquid crystallinity, the bisphenol A was replaced by an appropriate aromatic diol. Scheme 1 shows the polymerization reaction between the diglycidylether and the diol, and the mesogenic units used. The composition can be varied in such

Correspondence to: A. H. A. Tinnemans.

* Present address: General Electric Plastics BV, P.O. Box 117, 4600 AC Bergen op Zoom, The Netherlands.

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of 1,4-diglycidylbenzene, 1.86 g (10.0 mmol) of 4,4'-dihydroxybiphenyl, and 4 mL of DMAc was added. The reaction flask was blanketed with N₂ and heated to 160°C. When all monomers were dissolved, 0.04 mL (0.8 mol %) of ethyl(triphenylphosphonium) acetate (70% in methanol) was added as a base catalyst. A viscosity increase was observed within a few minutes, and compensated for by various additions of a few milliliters of solvent to maintain stirring. After 3 h, about 100 mg of 4,4'-dihydroxybiphenyl was added to cap any residual epoxy end groups. Then the reaction mixture was cooled to room temperature and diluted with DMAc to a 15 wt % polymer solution. The polymer was precipitated in water, under vigorous stirring with an Ultra Turrax mixer. The polymer was washed with methanol, filtered, and dried *in vacuo* at 60°C.

GPC

Gel permeation chromatography measurements were performed on a Waters GPC-2. A PLGel linear MIXED column 2× and a 500 Å precolumn were used. The column temperature was 70°C. Dimethylformamide (DMF) was used as eluant with a flow rate of 1 mL/min. Polystyrene samples were used for calibration. The output was detected with UV and RI.

DSC

Differential scanning calorimetry measurements were performed under a dry nitrogen flow on a DuPont 2200 DSC. Samples of 5–10 mg were placed in aluminium pans and heated with a rate of 20°C/min. After the first heating run (to 300°C) the samples were cooled with 20°C/min and a second heating run was performed. The peak of the endotherms was taken as the transition temperature.

Film Casting

Films were made by casting from an isotropic solution of 20 wt % polymer in DMAc. Prior to film casting the solution was filtered through a Teflon filter (Millipore, 5 μm pore size) to remove dust particles. Solutions were cast with a 200 μm doctor's knife onto a glass plate. The solvent was evaporated in an oven at 70°C, and films with a uniform thickness of 30 ± 2 μm were obtained.

DMTA

Dynamic mechanical measurements in tension were performed on an apparatus designed at

TNO. The apparatus has been described in detail in a publication of Damman and Buijs.⁸ Measurements were taken at temperature intervals of 4°C, and at frequencies of 1 and 10 Hz. The static strain was 0.25% and the dynamic strain amplitude was 0.03%.

Tensile measurements were performed according to ASTM D3379, on a small tensile testing machine designed at TNO, using a force transducer of Statham Instruments Inc.

A strain rate of 10%/min was applied.

RESULTS AND DISCUSSION

Synthesis and Molecular Weights

Table I shows the compositions and properties of the polyhydroxyethers synthesized from various combinations of hydroquinone (HQ) and biphenol (BP). Table II shows these data for the polyhydroxyethers synthesized from combinations of 4,4'-dihydroxy- α -methylstilbene (α MS) and BP.

The polymerization procedure was optimized to obtain polymers with a molecular weight high enough to make a strong, tough film. At first instance, the polymerization procedure according to the Shell patent² was followed. From the solvents mentioned in this patent, the ethers (dioxane, diglym) and methyl ethyl ketone did not work well because the polymer precipitated during polymerization; dimethylformamide (DMF) did keep the polymer in solution, and with an (insoluble) NaOH-pellet as catalyst, polymers **4** to **8** from Table I were prepared. However, very high molecular weights were not obtained in this way. A finer dispersed catalyst was thought necessary, and it was thought that DMF (a slightly basic solvent) was interfering with the reaction because the polymerization mixture turned brown. In dimethylacetamide (DMAc) the solution stayed clear, and with about 1 mol % finely crushed NaOH added as catalyst, polymers **1** and **2** were prepared, which had a much higher molecular weight. However, using slightly too much NaOH lead to gelation very quickly. As the amount of NaOH was difficult to control, another basic catalyst, ethyl(triphenylphosphonium) acetate (70% solution in methanol), was used. The added amount of this catalyst was easy to control, and polymers **3**, and **9** through **13** from Table II were successfully prepared in this way.

Another important finding was that a 5 mol % excess of diglycidylether relative to the aromatic diol resulted in a higher molecular weight than a

Table I Compositions and Properties of Polyhydroxyethers Based on 1,4-Dihydroxybenzene (HQ) and 4,4'-Dihydroxybiphenyl (BP)

Polymer No.	Diglycidylether of Aromatic Diol HQ/BP (mol/mol)	Aromatic Diol HQ/BP (mol/mol)	Total BP Content	M_n^a (M_w/M_n)	η_{inh}^b (dL/g)	T_g^c (°C)	T_m^c (°C)	Observations ^d
1	100/0	100/0	0	53000 (1.9)	0.80	68	amorphous	not LC
2	100/0	0/100	0.5	72000 (1.8)	0.78	98	246	not LC
3	50/50	0/100	0.75	37000 (1.6)	0.59	106	267	LC
4	0/100	64/36	0.68	—	0.48	102	255	not LC
5	0/100	57/43	0.715	63000 (2.0)	0.32	99	251/270	LC
6	0/100	50/50	0.75	58000 (2.0)	0.34	102	259/290	LC
7	0/100	33/67	0.83	—	0.33	113	285/309	LC
8	0/100	0/100	1	—	insoluble	not observed	305/336	—

^a Determined with GPC.^b C = 0.2 g/dL, at 25°C in DMAc.^c Determined with DSC.^d Using polarization microscopy.

1 : 1 stoichiometry. This can be explained by the reaction of the pendent hydroxy groups that are generated during polymerization. These secondary hydroxy groups, being less reactive than the primary hydroxy groups of the aromatic diol, may still react with a small part of the epoxy groups, and a partly branched polymer is obtained. A small degree of branching is practically inevitable when aiming at high molecular weights.⁹ Figure 1 shows the GPC curves of polymers **1**, **2**, and **3**. A small separate peak was observed at low elution volume, corresponding to high molecular weight. This small peak, which was observed for all the synthesized polyhydroxyethers, might represent the branched part of the polymer.

Thermal Characterization

Reinking et al.^{10–12} studied the influence of the connecting link between the aromatic rings in bisphenol on the glass transition temperature and barrier properties of polyhydroxyethers. The polyhydroxyether of bisphenol A, known as phenoxy, is an amorphous polymer with a T_g of 100°C. The polyhydroxyether based on hydroquinone had the lowest glass transition temperature in their series, 60°C.

Figure 2 shows the DSC thermograms of the polyhydroxyethers from Table I. The T_g of polymer **1** (based on 100% hydroquinone) was 68°C, which agrees reasonably well with the value

Table II Compositions and Properties of Polyhydroxyethers Based on 4,4'-Dihydroxybiphenyl (BP) and 4,4'-Dihydroxy- α -methylstilbene (α MS)

Polymer No.	Diglycidylether of Aromatic Diol BP/ α MS (mol/mol)	Aromatic Diol BP/ α MS (mol/mol)	Total BP Content	M_n^a (M_w/M_n)	η_{inh}^b (dL/g)	T_g^c (°C)	T_m^c (°C)	Observations ^d
9	100/0	75/25	0.875	23000 (1.6)	0.26	112	290/306	LC
10	100/0	50/50	0.75	31000 (1.5)	0.45	105	279/287	LC
11	100/0	25/75	0.625	25000 (1.6)	0.46	99	243	LC
12	100/0	0/100	0.5	38000 (1.6)	0.59	100	253	not LC
13	0/100	0/100	0	61000 (1.4)	0.61	86	188	not LC

^a Determined with GPC.^b C = 0.2 g/dL, at 25°C in DMAc.^c Determined with DSC.^d Using polarization microscopy.

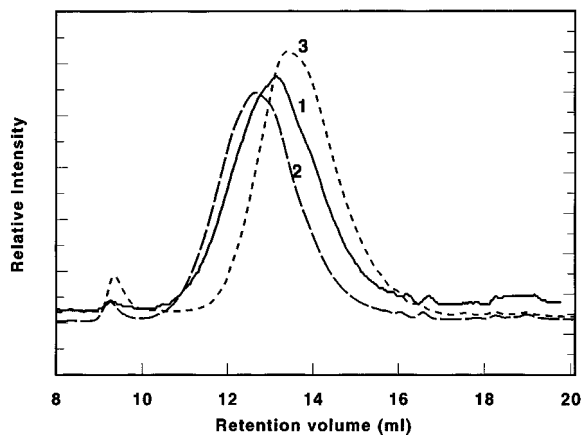


Figure 1 Gel permeation chromatograms of polymers 1–3.

found by Reinking et al. It is clearly seen that the glass transition and melting temperatures are increasing with increasing BP content. It is also observed that polymers 2 and 8 display higher melting enthalpies than the other polymers. This can be explained by the fact that these polymers are synthesized from a single diglycidylether and diol. Polymer 2 is, in fact, an alternating copolymer and polymer 8 a homopolymer. The other polymers are synthesized from mixtures of diols, which makes them irregular, random copolymers, resulting in a lower crystallinity. In Figure 3 the transition temperatures are plotted as a function of the BP content in the polymer. The glass transi-

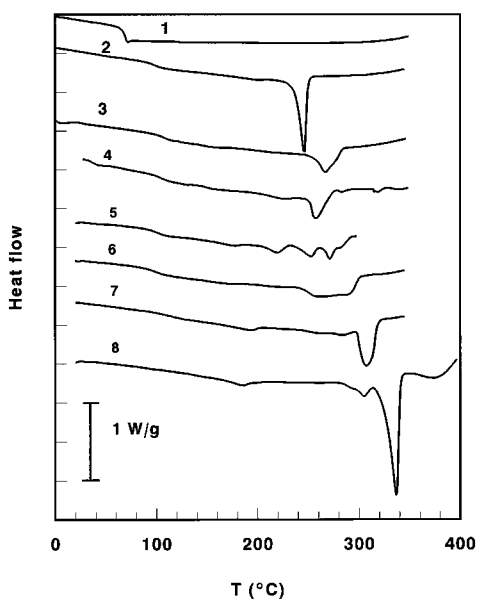


Figure 2 DSC thermograms of the polymers from Table I. Second heating runs are shown.

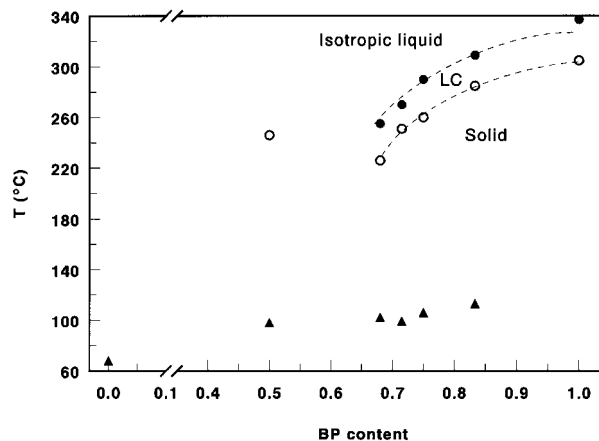


Figure 3 Glass transition (▲), melting (○), and isotropization (●) temperatures of polymers 1–8, as a function of the biphenyl (BP) content of the polymer.

tion temperature increased with increasing BP content. The polymer with 83% BP displayed a T_g of 113°C. The T_g of the polyhydroxyether based on 100% BP could not be observed, probably due to the high crystallinity of this polymer. The melting temperature also increased with increasing BP content. For the polyhydroxyethers containing 71.5% BP or more a liquid-crystalline phase was observed using polarized light optical microscopy. The liquid-crystalline range has roughly been indicated in Figure 3.

In search for other mesogenic groups, the α -methylstilbenic (α MS) unit is known to give liquid-crystalline oligo- and polyethers.^{13,14} Therefore, it was attempted to include α MS in the polyhydroxyethers (see Table II). The DSC thermograms are shown in Figure 4. Contrary to the expectation, α MS alone did not induce liquid-crystalline behavior. Liquid-crystalline melts were observed only when the polymer contained 62.5% or more BP. An increasing α MS content lowers the melting and glass transition temperature. From Tables I and II, it is clear that the biphenol has a major influence on the formation of a liquid-crystalline phase in these polyhydroxyethers.

Drawing and Mechanical Characterization

When the inherent viscosity of the polymer was higher than 0.5 dL/g, coherent films could be prepared. Therefore, only films of polymers 1–3, and 12 were cast from solution and drawn on a hot shoe. No film was made of polymer 13 because of solubility problems. The drawing process was performed in such a way to induce a high degree of orientation, and thus a high tensile modulus.

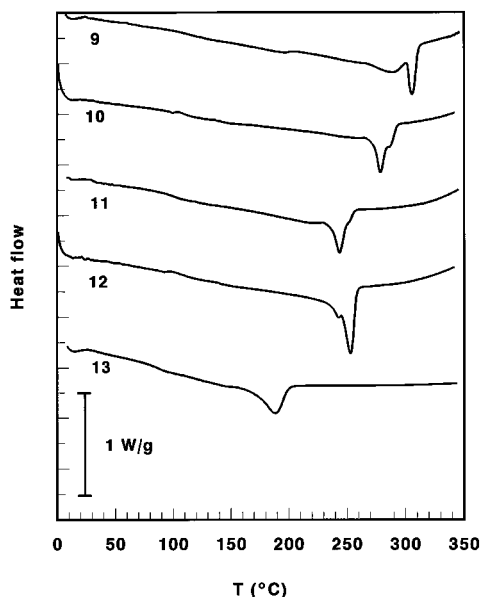


Figure 4 DSC thermograms of the polymers from Table II. Second heating runs are shown.

This means that the film was drawn just above or at the glass transition temperature to prevent fast relaxation of the chains. The maximum draw ratio (λ , final length/original length) was higher for polymers with higher inherent viscosity. A maximum λ of 3.5 was obtained at $\eta_{inh} = 0.8$ dL/g. Table III shows the static tensile modulus, tensile strength, and strain at break for as-cast and drawn films of polymers **1–3**, and **12**. The modulus of an as-cast film varies from 1 to 2.3 GPa, and of the film with maximum draw ratio from 2 to 5 GPa. This indicates that the chains have not been oriented to a large extent. A multiple-step

drawing procedure, in which each step was performed at successively higher temperatures, did not lead to a higher modulus of the films. Polymer **3** was expected to orient better than the rest, because it showed a liquid-crystalline phase. However, no substantial differences between the polymers were found. One of the reasons for the limited orientability of these polymers might be the relatively long flexible part in the chain, which comprises two oxygen atoms and three carbon atoms. This accounts for a fast relaxation of this part of the chain. Another reason that could prevent the achievement of a high degree of orientation is the fact that the polymer is probably partly branched, as discussed before.

As-cast and drawn films were further characterized by dynamic mechanical measurements. Figure 5 shows the dynamic tensile modulus and loss tangent (at 10 Hz) against temperature, of the polymers **1–3**, and **12**. The dynamic modulus at 10 Hz and room temperature varies from about 2–3 GPa for as-cast films to about 5 GPa for drawn films. The clearly visible T_g in the temperature range of 110 to 150°C confirms the DSC results. Depending on composition and draw ratio, several secondary relaxations can be observed at lower temperatures. Only a few studies have appeared concerning the internal mobilities of polyhydroxyethers.^{10,13} Most of these polyhydroxyethers show two secondary relaxations. The lowest temperature relaxation, at about -70°C , is assumed to be caused by the aliphatic chain part between the ether linkages.¹⁰ A secondary relaxation at about 50°C was ascribed to a rotation of the aromatic rings.¹³ It is to be expected that similar mechanisms are responsible for the relaxations found in the polymers described here.

Table III (Static) Tensile Modulus, Tensile Strength, and Strain at Break of As-Cast and Drawn Films of a Number of Polyhydroxyethers

Polymer Number and Draw Ratio		E (GPa, at 25°C , 10 Hz)	σ (MPa)	ε_b (—)
1	$\lambda = 1$ (as-cast)	1.0	12	— ^a
	2.9	2.0	104	0.07
2	$\lambda = 1$ (as-cast)	2.1	52	0.11
	3.3	5.0	171	0.067
3	$\lambda = 1$ (as-cast)	2.3	54	0.041
	2.6	3.1	110	0.092
	3.5	4.5	150	0.073
12	$\lambda = 1$ (as-cast)	1.9	37	0.042
	2.5	3.2	83	0.086
	3.0	4.9	170	0.068

^a The film doesn't break, but yields.

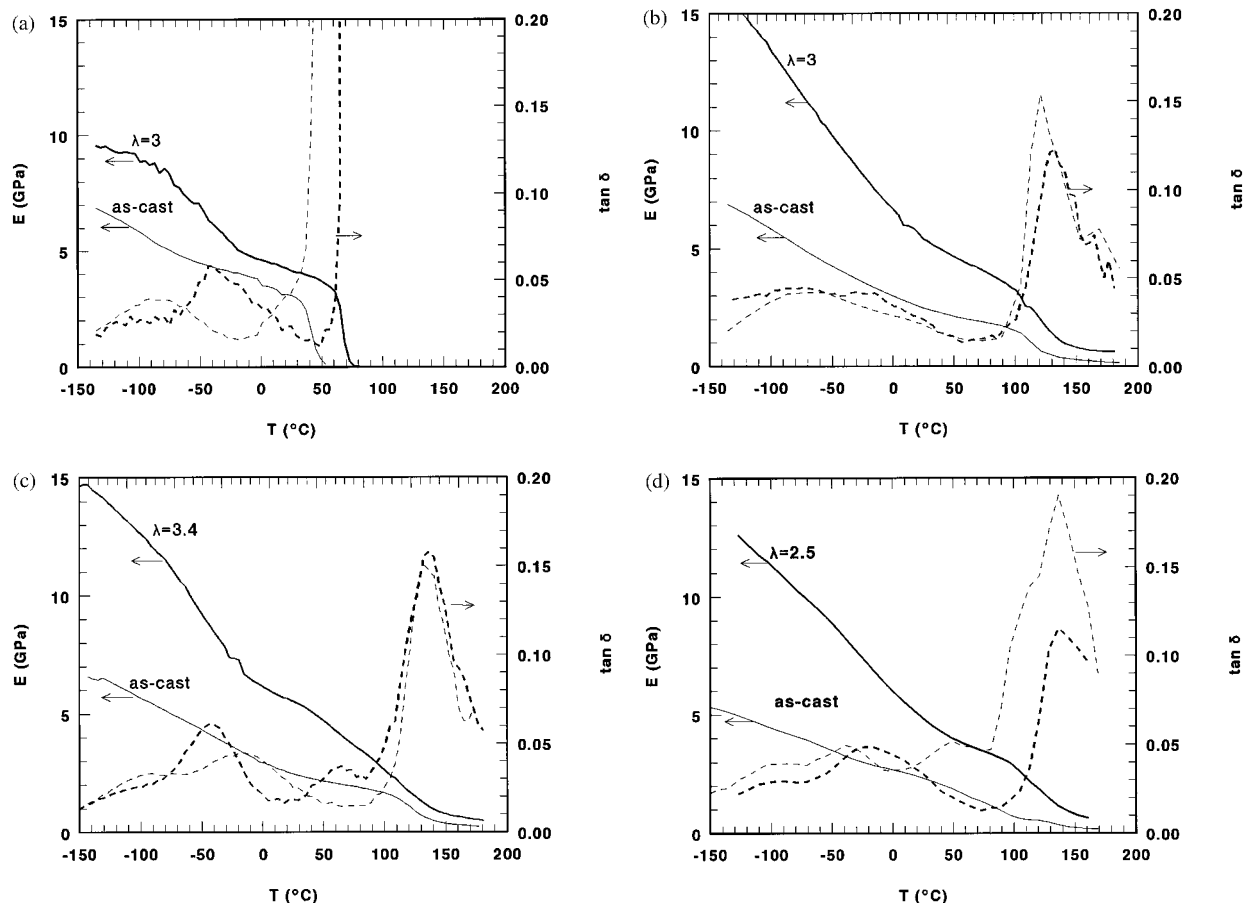


Figure 5 Dynamic tensile modulus (E , —) and loss tangent ($\tan \delta$, ----) at 10 Hz, as a function of temperature, of (a) polymer **1**; (b) polymer **2**; (c) polymer **3**; (d) polymer **12**. For each polymer the curves of an as-cast (thin lines) and a drawn film (bold lines) are shown.

CONCLUSIONS

The synthesis of polyhydroxyethers was optimized to give high molecular weight polymers, which show a thermotropic liquid-crystalline phase when a sufficient amount of biphenyl units has been incorporated in the chain. The liquid-crystalline polyhydroxyethers could be attractive candidates to reinforce thermoplastics, both because of their liquid crystallinity, which favor the formation of oriented structures, and because of the presence of potentially reactive hydroxy groups. These could react with functional groups in the matrix polymer, and in this way improve the adhesion between fiber and matrix through covalent bonds. Four of the synthesized polyhydroxyethers have been mechanically characterized. Judging from the tensile modulus, a high degree of orientation was not obtained in solution-cast and subsequently drawn films. Nevertheless, because of

their proven chemical interaction,³⁻⁵ some of the discussed polyhydroxyethers might be interesting to blend with polyesters. An interesting combination would be polymer **3** with poly(ethylene terephthalate) (PET); the processing range of PET coincides with the liquid-crystalline range of polymer **3**, discussed in this article.

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