

Unsaturated *Para*-Linked Aromatic LC Polyesters: Thermotropic and Lyotropic Systems

MIKAEL SKRIFVARIS* and HANS-WERNER SCHMIDT†

Materials Department, College of Engineering, University of California, Santa Barbara, California 93106

SYNOPSIS

Liquid-crystalline thermosets (LCT) are a new class of materials which combine typical properties of LC polymers with those of conventional thermosets. This article reports on the development of a *lyotropic LC thermoset* (LLCT) in which the solvent is a vinyl monomer. Such an LLCT is expected to have several advantages compared to conventional unsaturated polyester resins. The synthesis and characterization of a variety of novel substituted *para*-linked aromatic polyesters and copolyesters containing unsaturated fumaroyl units is presented. The thermal and liquid crystal properties were investigated. It is demonstrated that it is possible to prepare a lyotropic LC solution in styrene. These lyotropic solutions are capable of thermal crosslinking by the addition of a free-radical initiator. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Liquid-crystalline thermosets (LCT) are a new class of materials which combine typical properties of thermotropic LC polymers with those of conventional thermosets. Their network structure is based on rigid-rod or extended-chain segments which are crosslinked in three dimensions. LCTs are expected to offer such capabilities as lower viscosity during processing, improved coefficients of thermal expansion, and increased fracture toughness when crosslinked.¹ Especially in macroscopically oriented samples, the LC order may be preserved after crosslinking, thus leading to enhanced properties perpendicular to the orientation direction. So far, most of the reported LCTs are thermotropic. Thermotropic LCTs (TLCTs) are functionalized rigid-rod polymers, oligomers, or monomers which are crosslinked within the mesophase, resulting either in isotropic or anisotropic network structures. TLCTs with crosslinkable units in the main chain or as end groups have been reported. Typical functional

crosslinkable units in the main chain are fumaroyl,² cinnamoyl,³ *p*-phenylenediacryl,^{3d,4} or stilbene units.⁵ Functional units which have been used as end groups are maleimide,⁶ epoxy,⁷ vinyl,⁸ isocyanate,⁹ acetylene,¹⁰ or acrylate groups.¹¹

This article reports on the development of lyotropic LC thermosets (LLCTs) in which the solvent is a vinyl monomer. In LLCTs, the crosslinking occurs in a lyotropic solution between the extended chains of a rodlike unsaturated polymer and the polymerizable solvent. To our knowledge, such a system has not been reported so far. An LLCT could be expected to have several advantages compared to conventional unsaturated polyester resins. Commercial styrene-based resins contain typically a flexible chain unsaturated polyester dissolved in up to 35–50 wt % styrene. Styrene participates not only in the crosslinking reaction, but also acts as a solvent to lower the viscosity during processing.¹² Due to the high volatility of styrene, up to 2–5 wt % of the initial amount of styrene can evaporate during an open mold process.¹³ Therefore, unsaturated polyester resins with a low styrene content are desirable. As a consequence of the lower styrene content, at a comparable molecular weight of the unsaturated polyester, a resin with higher viscosity results, which is more difficult to process. Particularly at this point, an LLCT could afford a substantial improvement.

* Permanent address: Neste Oy, Corporate R&D, P.O. Box 310, FIN-06101 Porvoo, Finland.

† To whom correspondence should be addressed at Universität Bayreuth, Makromolekulare Chemie I, D-95440 Bayreuth, Germany.

Journal of Applied Polymer Science, Vol. 55, 1787–1795 (1995)

© 1995 John Wiley & Sons, Inc.

CCC 0021-8995/95/131787-09

Generally, the viscosity of a lyotropic solution is lower compared to an isotropic solution, although the polymer concentration is higher.¹⁴ Therefore, it should be possible to decrease the styrene content while maintaining a low viscosity resin, which is easily processable at low styrene emissions, thus fulfilling the required property profile.

It will be demonstrated that it is possible to obtain a sufficient high solubility for some polyesters in styrene and to prepare a lyotropic styrene-based thermoset resin. The lyotropic solution is capable of undergoing thermal crosslinking by the addition of a free-radical initiator.

To approach an LLCT based on styrene, we report on the synthesis of a variety of novel *para*-linked aromatic polyesters and copolyesters containing unsaturated fumaroyl units. To achieve the desired solubility in styrene, structural modification concepts such as the incorporation of bulky lateral substituents and noncoplanar biphenylene units were applied.¹⁵ Bilibin et al.^{2a} reported on semiflexible thermotropic polyesters containing fumaroyl units within the mesogenic unit, while Rätzsch et al.^{2b,c} worked with semiflexible thermotropic polyesters with fumaroyl units in the flexible part of the polyester. In contrast to the unsaturated LC polyesters described by Bilibin and Rätzsch, the polyesters in this work contain no flexible aliphatic spacers. This is important in order to maintain maximum chain stiffness, particularly in solution.

EXPERIMENTAL

Materials

Fumaroyl chloride (Aldrich, 95%) was distilled in vacuum and stored under nitrogen. Phenylhydroquinone (Aldrich, 97%) was purified by sublimation. *t*-Butylhydroquinone (Eastman Kodak, 98%) was recrystallized from dry toluene under nitrogen. Hydroquinone (Aldrich, 99+ %) and *p*-toluoyl chloride (Aldrich, 98%) were used without further purification. The syntheses of 2-phenethylhydroquinone and 2,2'-dimethylbiphenyl-4,4'-diol were performed according to literature procedures developed by Brüggling et al.¹⁶ and Schmidt and Guo.¹⁷ All other reagents were used as received.

Characterization

Solution viscosity was measured using a Lauda Automatic Viscoboy with 0.5 and 1.0 g/dL solutions in chloroform or trifluoroacetic acid at 25°C. Number- and weight-average molecular weights were deter-

mined in chloroform with a Spectra-Physics HPLC System equipped with two PSS gel columns with 100,000 and 1000 Å pore sizes and a UV detector (254 nm). Polystyrene standards were used for the calibration and octaphenylcyclotetrasiloxane (Aldrich) as the internal standard. Thermogravimetric analysis and differential scanning calorimetry were carried out with a Mettler TA 3000 System. The heating and cooling rates were 10°C/min. The analysis was done under nitrogen. Polarization microscopy was performed with a Nikon Microphot-FX microscope, equipped with a Mettler FP 5 hot stage and a Nikon 35 mm camera.

Polymer Synthesis

Interfacial Polycondensation of Polyesters 1–6

H₂O, 20 mL, and chloroform, 75 mL, were placed in a blender flushed with nitrogen. Benzyltriethylammonium chloride, 230 mg (10 wt % of the theoretical polymer yield), was used as a phase-transfer catalyst. The diol, 5 mmol, was diluted in 20 mL degassed 0.5N NaOH under a nitrogen atmosphere and transferred to the blender as quickly as possible. An equimolar amount of fumaroyl chloride, diluted with a small amount of dry chloroform (prior dried over P₄O₁₀), was added to the chloroform phase. The reaction mixture was vigorously stirred for approximately 10 min. The resulting polyester was isolated by the addition of ethanol. The polyester was purified by dissolving in THF, precipitation in ethanol, and finally dried in vacuum at 60°C overnight. Polymer **5** is a copolyester synthesized from fumaroyl chloride and 1 : 1 *t*-butylhydroquinone/phenylhydroquinone, also prepared by interfacial polycondensation. The ratio of the components was determined quantitatively by ¹³C-NMR (270 MHz, CDCl₃, TMS).

Melt Polycondensation of Polyester 2b

This polyester was also synthesized from fumaroyl chloride and *t*-butylhydroquinone via a melt polycondensation. In a polycondensation reactor, equipped with a twin-screw mixer and nitrogen inlet, 14.96 g (90 mmol) *t*-butylhydroquinone was melted. To regulate the molecular weight of the polyester, 0.28 g (1.8 mmol) of a monofunctional end-capper, *p*-toluoyl chloride, was added to the melt. The coupling of the end-capper was allowed to proceed for 1 h at 145°C; then, 13.77 g (90 mmol) fumaroyl chloride was added dropwise. After 4 h at 170°C, a viscous, opaque melt had formed. The polyester was dissolved in warm chloroform, treated with activated

Table I. Characterization of the Polyesters 1–6

Sample	Yield (%)	Viscosity ^a η_{inh} (dL/g)	M_n^b (g/mol)	Polydispersity ^c	IR (cm ⁻¹) ^d	
					ν (C=O)	ν (C=C)
1 ^e	68	—	—	—	1734	965
2a	79	0.30	2,300	2.7	1738	965
2b	63	0.30	3,000	4.0	1740	965
3	77	0.29	4,600	3.6	1736	971
4	61	0.63	6,300	4.1	1736	972
5	67	0.32	4,000	2.8	1736	965
6	66	2.09 ^f	34,700	5.0	1736	965

^a Inherent viscosity in chloroform at 25°C at a concentration of 0.5 g/dL.

^b Determined by GPC in chloroform with polystyrene calibration.

^c Polydispersity = M_w/M_n .

^d Measured in KBr.

^e Insoluble in chloroform or trifluoroacetic acid.

^f Measured in trifluoroacetic acid at 25°C and 1.0 g/dL.

charcoal, and precipitated in cold ethanol. The precipitation procedure was repeated once. The polyester was finally dried in vacuum at 60°C overnight. All data for the synthesis and characterization of the polyesters 1–6 are summarized in Table I.

RESULTS AND DISCUSSION

Synthesis and Characterization of Unsaturated LC Polyesters

The synthesis of a series of unsaturated *para*-linked aromatic polyesters 1–6 containing fumaroyl units is described. To maintain a maximal chain stiffness, no aliphatic spacer was incorporated. The chemical structures of the synthesized polyesters are shown in Figure 1. To achieve a certain solubility of the polyesters, to lower the melting temperature, and to decrease the degree of crystallinity, several concepts of structural modifications were applied. Polyesters 2–4 were structurally modified by using bulky lateral substituents, such as *t*-butyl-, phenyl-, and phenethyl substituents. Polyester 5 is a copolyester based on *t*-butylhydroquinone and phenylhydroquinone. The molecular composition of the copolyester 5 was determined by ¹³C-NMR spectroscopy. Polyester 6 contains a 2,2'-dimethyl-substituted biphenylene unit, which has a noncoplanar conformation.

Polyesters 1–6 were synthesized by an interfacial polycondensation. The polycondensation reaction is schematically shown in Figure 2. This polymerization method was selected to avoid potential degradation or side reactions of the fumaroyl double bond. The interfacial polycondensation was carried out

according to a standard technique, involving the reaction of disodium phenolate with fumaroyl chloride in a two-phase system of water and chloroform. As phase-transfer catalyst, benzyltriethylammonium

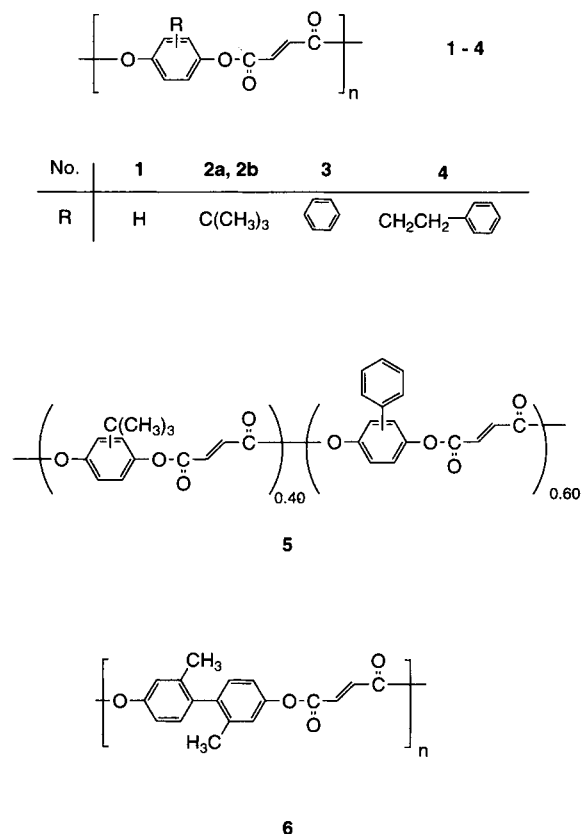
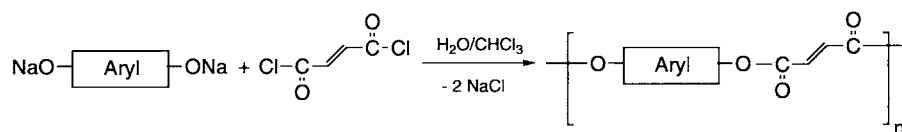
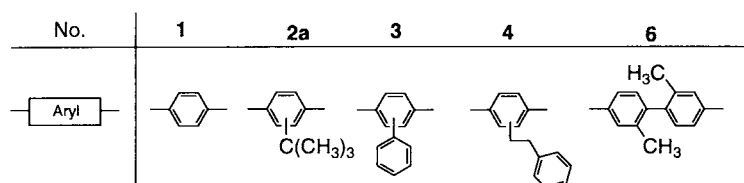
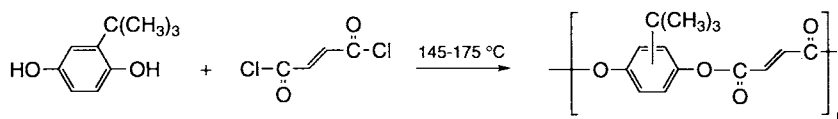


Figure 1 Chemical structure of fumaroyl-based aromatic polyesters 1–6.

Interfacial Polycondensation

1 - 6

**Melt Polycondensation**

2b

Figure 2 Synthesis of fumaroyl-based aromatic polyesters **1–6** by interfacial and melt polycondensation.

chloride was used. Once the thermal transitions and degradation properties of the polyesters were known (see below), we prepared polyester **2b** by a melt polycondensation directly from *t*-butylhydroquinone and fumaryl chloride. The highest reaction temperature applied was 170°C. Under these reaction conditions, no degradation or crosslinking reactions were observed. Compared to the interfacial polycondensation, a melt polycondensation allows the synthesis of larger quantities. All soluble polyesters were characterized by viscosity and GPC; the data are compiled in Table I.

Unsubstituted polyester **1** could not be dissolved in common organic solvents, whereas the laterally substituted polyesters **2–5** could be easily dissolved in organic solvents such as chloroform. Polyester **6** containing the noncoplanar biphenylene unit was not soluble in chloroform, but could be dissolved in trifluoroacetic acid. The inherent viscosities were measured for polyesters **2–5** in chloroform and ranged from 0.29 to 0.63 dL/g (see Table I). The weight-average molecular weights which were determined by GPC (chloroform as a solvent and com-

pared to polystyrene standards) were found to be between 6100 and 26000 g/mol for polyesters **2–5**. The distributions were monomodal and the poly-

Table II Thermal Properties of Polyesters **1–6** as Investigated by TGA, DSC, and Polarization Light Microscopy

Sample	TGA ^a (°C)	T_g^b (°C)	T_m (°C)	T_{cl} (°C)	LC Phase ^e
1	250	40	— ^c	— ^c	—
2a	260	100	—	245–250 ^d	Nematic
2b	310	100	—	260–270 ^d	Nematic
3	320	85	230	250–260 ^d	Nematic
4	280	50	—	265–275 ^d	Nematic
5	300	90	—	245–250 ^d	Nematic
6	320	115	— ^c	— ^c	—

^a Temperatures reported for 5% weight loss.

^b Data reported from second heating run.

^c No melting observed before decomposition started.

^d Clearing temperature (T_{cl}) within the decomposition range.

^e Determined by polarization light microscopy.

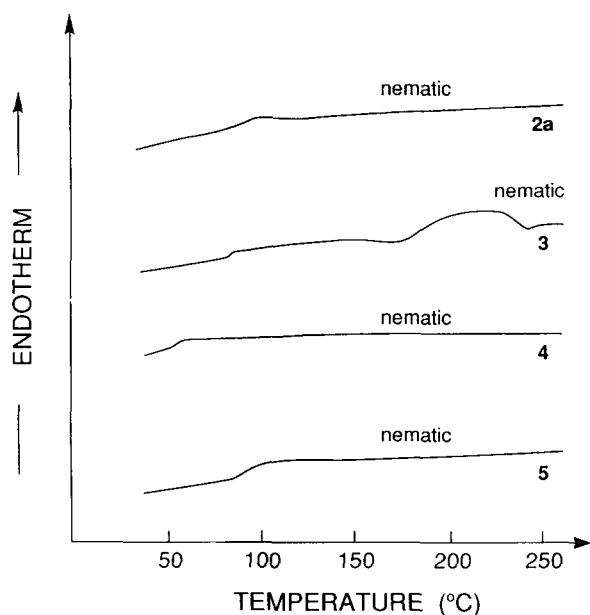


Figure 3 DSC heating curves of polyesters **2a**, **3**, **4**, and **5**. Second heating run, 10°C/min; samples cooled 10°C/min.

dispersity ranged from 2.7 to 5.0. Polyester **2a** and **2b**, synthesized by interfacial and melt polycondensation, have the same inherent viscosity of 0.30 dL/g. The GPC analysis revealed for the interfacial po-

lycondensation a lower average molecular weight but a significantly broader molecular weight distribution for polyester **2b** prepared by melt condensation. Polyester **6** has an inherent viscosity of 1.09 dL/g in trifluoroacetic acid at 25°C.

Thermal properties of the polyesters are summarized in Table II. The thermal degradation was investigated by dynamic TGA. For the polyesters, a 5% weight loss (under nitrogen) was observed between 250 and 320°C. Phase transition temperatures were determined by DSC up to 255°C and the results from the second heating are shown in Figure 3. Depending on the substitution, the observed glass-transition temperatures ranged from 40 to 115°C. Polyesters **2a**, **2b**, and **3** with rigid substituents have higher glass transition temperatures compared to polyester **4** with the flexible phenethyl substituent. It is known from other saturated LC polyesters that the flexible phenethyl substituent acts as an internal plasticizer and, hence, lowers the glass transition temperatures.¹⁶ Copolyester **5** shows a glass transition temperature at 90°C, which falls between the glass transition temperatures for the corresponding homopolyesters. No other transitions were observed for the polyesters except for the *t*-butyl substituted polyester **3**; this polyester exhibits a broad endothermic transition from 180 to 240°C. Unsubstituted polyester **1** and polyester **6** contain-

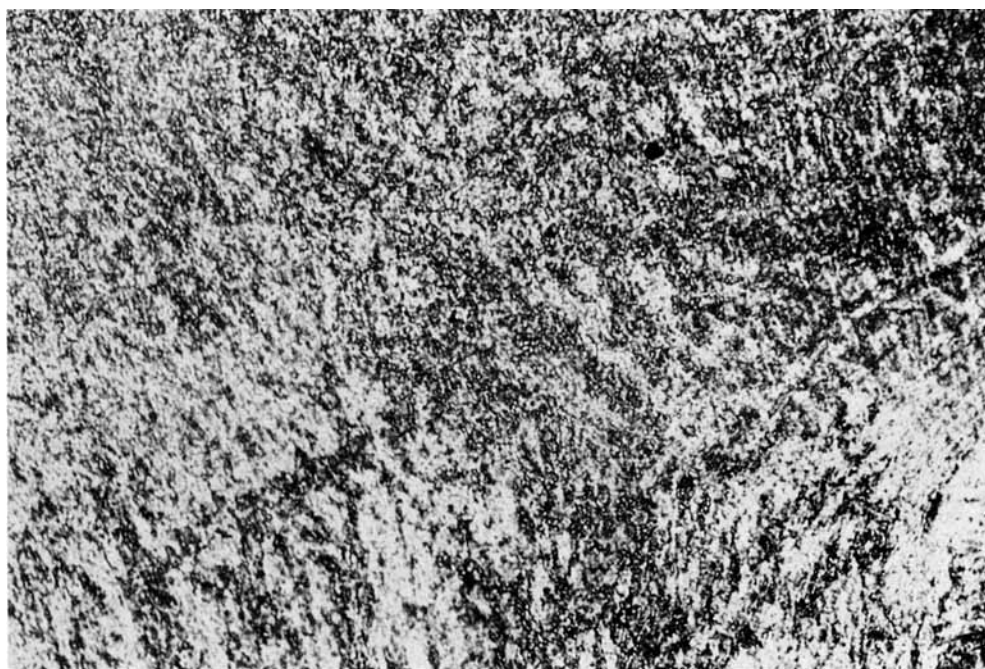


Figure 4 Optical micrograph between crossed polarizers of polyester **4** (at 185°C), showing a nematic texture (magnification 200×).

Table III Solubility of Polyesters 1–6 at Room Temperature in Styrene, Methyl Methacrylate, and Vinyl Acetate

Sample	Styrene		Methyl Methacrylate		Vinyl Acetate	
	5 Wt %	20 Wt %	5 Wt %	20 Wt %	5 Wt %	20 Wt %
1	–	–	–	–	–	–
2a	+	+	+	+	+	+
3	–	–	–	–	–	–
4	+/-	–	+/-	–	+/-	–
5	+	+	+	+	+	–
6	–	–	–	–	–	–

+: soluble; +/-: partly soluble; -: not completely soluble or partially swollen.

ing the noncoplanar biphenyl unit did not melt before decomposition started. To detect LC behavior, the meltable polyesters were studied by light microscopy between crossed polarizers. It was found that polyesters **2a**, **2b**, **4**, and **5** are thermotropic LC above their glass transition temperature, as nematic textures were observed. As an example, the texture of polyester **4** at 185°C is shown in Figure 4. Upon shearing, the nematic melt flows easily. At 150°C, clearly above its T_g , polyester **3** is not completely molten and becomes fluid at 230°C. Above this temperature, a nematic phase is also observable. All polyesters show broad clearing transitions in the range of 255–275°C, in which simultaneous decomposition and crosslinking occurs.

Solution Properties of Unsaturated Polyesters in Vinyl Monomers

With the objective to use these unsaturated LC polyesters as materials for thermosets, we explored the solubility of the polyesters in common vinyl monomers such as styrene, methyl methacrylate, and vinyl acetate. Styrene is the most commonly used crosslinking monomer in unsaturated polyester resins. The solubility was tested at polymer concentrations of 5 and 20 wt % at room temperature. The results are compared in Table III. As expected, polyesters **1** and **6** are soluble in these monomers. The best solubility at 5 and 20 wt % was observed for polyester **2** with the *t*-butyl substituent. Surprisingly, polyester **3** was not soluble even in styrene under these conditions. However, copolyester **5** is soluble in all three vinyl monomers. The phenethyl-substituted polyester **4** swells at 5 wt % and is not completely soluble. These results demonstrate that the *t*-butyl group is by far the best substituent to achieve solubility in these monomers. Therefore,

styrene was chosen to investigate the phase behavior and the potential of lyotropism.

Lyotropic Solutions of the *t*-Butyl-substituted Polyester **2b** in Styrene

Polyester **2b**, synthesized by melt polycondensation, was used for the investigation of lyotropic behavior in styrene. One gram samples with 5–95 wt % of **2b** in styrene were prepared and investigated by light microscopy between crossed polarizers. The solutions were prepared by the following method: The polyester and styrene were accurately weighed in 20 mL glass vials. To promote homogeneous starting conditions, a small amount of methylene chloride was added; then, the vials were sealed and incubated at 50°C for 30 min. The methylene chloride was carefully evaporated at room temperature until a constant sample weight was reached. The final composition of the samples was determined by thermogravimetry. Figure 5 compares the thermogravimetric analysis of polyester **2b** with a styrene solution. No evaporation of residual methylene chloride is observable; during the evaporation procedure styrene partially evaporates. Styrene evaporates completely at temperatures from 100 to 200°C, and the recorded weight loss (Δ) corresponds to the styrene concentration in the mixture. Therefore, all concentrations used in the following are based on the measured TGA results.

Temperature-dependent optical investigations by light microscopy between crossed polarizers revealed the softening temperatures of the mixtures. Two separate experiments were performed to record the softening point as a function of the polyester concentration. The solutions prepared in the glass vials as described above were investigated (Fig. 6, □). Additionally, the methylene chloride was not evapo-

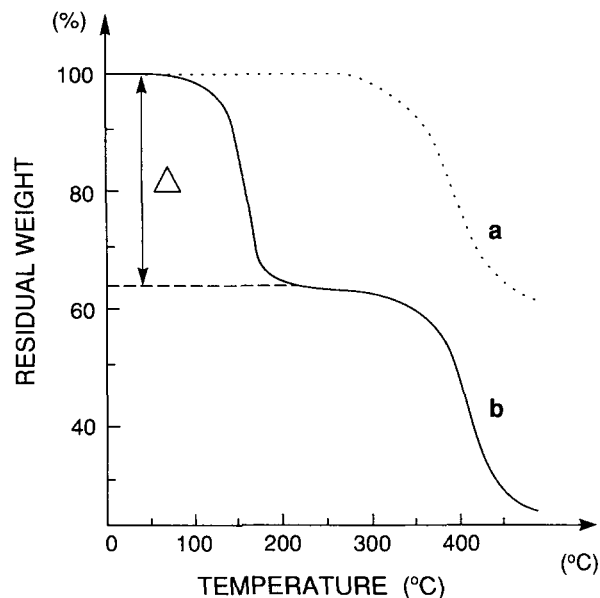


Figure 5 Thermogravimetric determination of the styrene content in a mixture of polyester **2b**/styrene. Neat polyester (**a**, dashed line), mixture containing 37 wt % styrene (**b**, solid line); (Δ) represents the styrene content. Heating rate of 10°C/min, under nitrogen.

rated in a separate step, but during the investigation using the hot stage on the microscope table (Fig. 6, \blacktriangle). In Figure 6, the softening point temperature of the samples is plotted vs. their polyester concentration in styrene. In some cases, anisotropic gels and liquid crystallinity was observed. At concentrations below approximately 50 wt % and at room temperature, the samples form an isotropic gel, which melts into an isotropic liquid upon raising the temperature. At high polyester concentrations, the samples are birefringent gels at room temperature. These gels transform into lyotropic liquid crystalline solutions at elevated temperatures. At a polyester concentration of 90 wt %, the softening point is around 90°C and gradually decreases with increasing styrene concentration. Figure 7(a) shows the birefringent nematic texture at a polyester content of 63 wt % at 80°C, and a similar texture can be seen in Figure 7(b), at a polyester content of 83 wt % at 70°C. Both nematic solutions have very low viscosity compared to the thermotropic polyesters. This demonstrates for the first time that it is possible to obtain sufficiently high styrene-soluble LC polyester which forms a lyotropic LC phase. By heating the solutions above 140°C, the styrene evaporates and the thermotropic nematic texture described above can be seen.

The first studies indicate that it is possible to

crosslink the lyotropic solutions. A 60 wt % sample of polyester **2b** in styrene was prepared according to the two-stage process described above with methylene chloride. The polyester was mixed with the appropriate amount styrene in a twin-screw mixer, and a slight amount of methylene chloride was added to homogenize the sample. Benzoyl peroxide (1 wt %) was added and excess methylene chloride was removed by evaporation at 40°C. Thin films of the obtained mixture were prepared in a Carver Laboratory press at 100°C and cured. The obtained films were brittle, but did not dissolve or even swell in chloroform, which indicates that substantial crosslinking had occurred. Further investigations of the detailed curing conditions and materials properties are in progress.

CONCLUSIONS

We synthesized unsaturated polyesters from fumaroyl chloride and *t*-butyl-, phenyl-, and phenethylhydroquinones. The *t*-butyl and the phenethyl-substituted polyesters are thermotropic nematic liquid crystals above their glass transition temperatures, while the phenyl-substituted polyester shows a nematic texture above the melting point. The *t*-

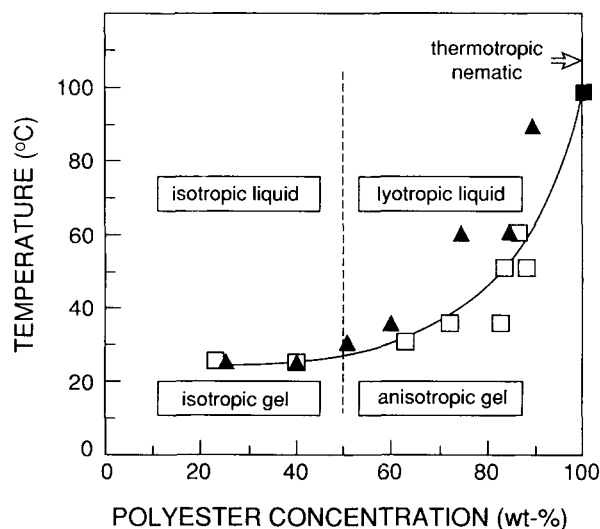


Figure 6 Softening temperature of polyester **2b**/styrene mixtures determined by optical microscopy. The critical concentration for the onset of a lyotropic phase (dashed line) is in the range of 50 wt %. (\square) Solutions separately prepared by evaporation of CH_2Cl_2 in a glass vial; (\blacktriangle) solutions prepared by evaporation of CH_2Cl_2 on a microscopy glass slide; (\blacksquare) glass transition temperature of polyester **2b**.

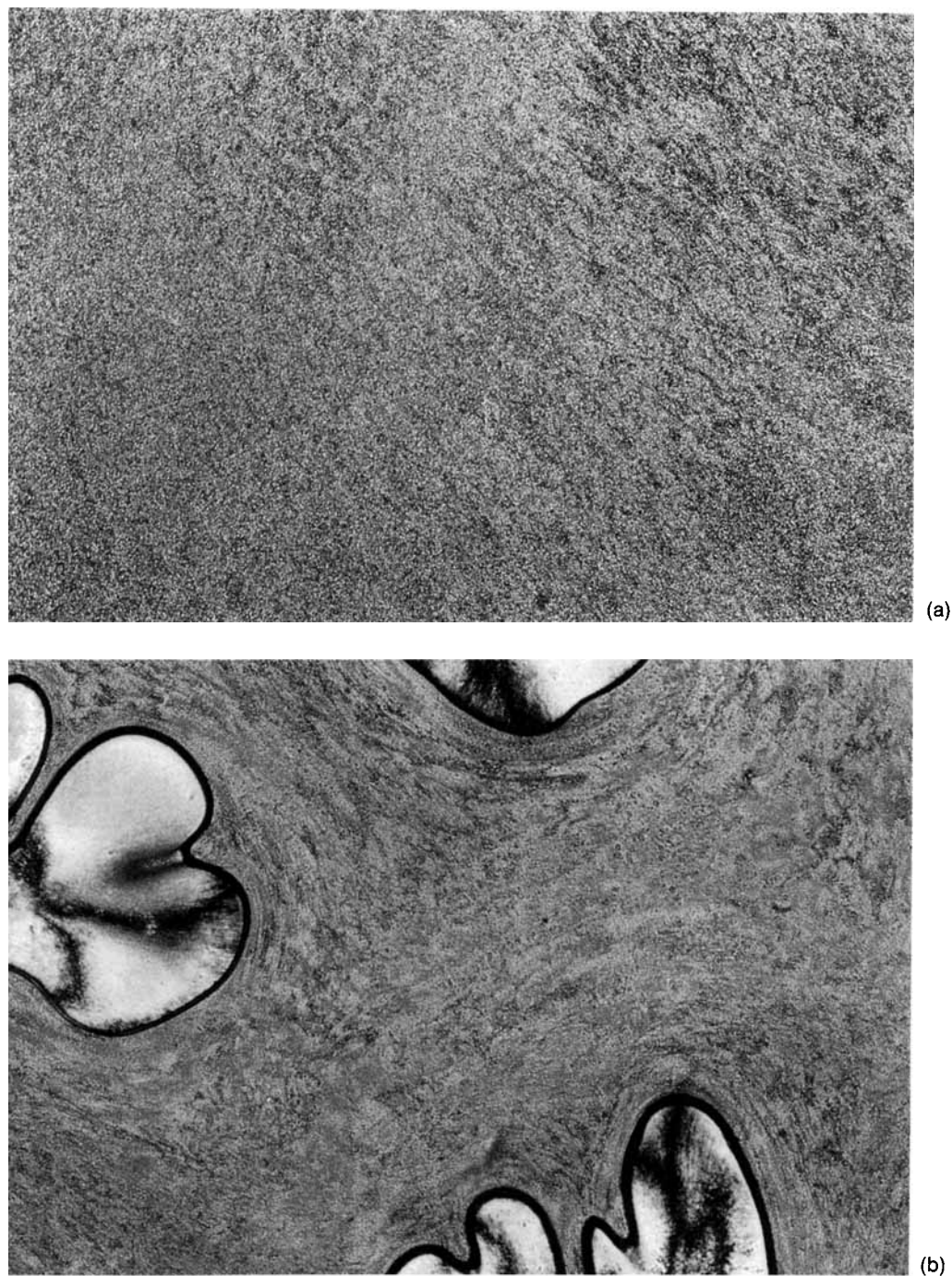


Figure 7 Optical micrograph between crossed polarizers of polyester **2b** in styrene (magnification 200 \times): (a) polyester content 63 wt %, temperature 80°C; (b) polyester content 83 wt % at 70°C.

butyl and the phenylethyl-substituted polyesters and a copolyester of *t*-butyl- and phenylhydroquinone are soluble in common vinyl monomers. At least, the *t*-butyl-substituted polyester forms a lyotropic

phase in styrene above 50 wt % polyester. In preliminary experiments, such a lyotropic system could be processed into a film and crosslinked with benzoyl peroxide.

This study was possible by a grant from Neste Oy, Finland. Dr. Andreas Greiner, University of Marburg, Germany, is gratefully acknowledged for supplying 2-phenethylhydroquinone. We thank Dr. Reiner Giesa for valuable suggestions and his help in the preparation of the manuscript.

REFERENCES

1. For a recent review, see: G. G. Barclay and C. K. Ober, *Prog. Polym. Sci.*, **18**, 899 (1993).
2. (a) A. Y. Bilibin, V. V. Zuev, and S. S. Skorokhodov, *Makromol. Chem. Rapid Commun.*, **6**, 601 (1985). (b) M. Rätzsch and K. Peter, *Makromol. Chem.*, **191**, 1021 (1990). (c) K. Peter, R. Peter, and M. Rätzsch, *Makromol. Chem.*, **192**, 2901 (1991). (d) T. Galcera, A. Fradet, and E. Marechal, *Makromol. Chem. Macromol. Symp.*, **64**, 33 (1992).
3. (a) C. H. Li, W.-W. Lai, K. H. Hsu, and T.-C. Chang, *J. Polym. Sci. Polym. Chem.*, **31**, 27 (1993). (b) D. M. Haddleton, D. Creed, A. C. Griffin, C. E. Hoyle, and K. Venkataram, *Makromol. Chem. Rapid Commun.*, **10**, 391 (1989). (c) H. Elsner and H. Ritter, *Makromol. Chem. Rapid Commun.*, **8**, 595 (1987). (d) F. Navarro, *Macromolecules*, **24**, 6622 (1991).
4. (a) C.-H. Li, K.-Y. Hsu, and T.-C. Chang, *J. Polym. Sci. Polym. Chem.*, **31**, 1119 (1993). (b) T. Ikeda, H. Itakura, C. Lee, F. M. Winnik, and S. Tazuke, *Macromolecules*, **21**, 3536 (1988).
5. (a) M. Carotenuto and P. Iannelli, *Macromolecules*, **25**, 4373 (1992). (b) G. W. Calundann, H. A. A. Rasoul, and H. K. Hall, U.S. Pat. 4,654,412 (March 27, 1986/March 31, 1987) (to Celanese Corp.).
6. A. E. Hoyt, B. C. Benicewicz, and S. J. Huang, in *Liquid Crystalline Polymers*, R. A. Weiss and C. K. Ober, Eds., ACS Symposium Series 435, American Chemical Society, Washington, DC, 1990.
7. (a) G. C. Barclay, S. G. McNamee, C. K. Ober, K. I. Papathomas, and D. W. Wang, *J. Polym. Sci. Polym. Chem.*, **30**, 1845 (1992). (b) B. A. Rozenberg and L. L. Gureva, *Polym. Mater. Sci. Eng.*, **66**, 162 (1992).
8. H. Andersson, U. W. Gedde, and A. Hult, *Polymer*, **33**, 4014 (1992).
9. (a) W. Mormann and M. Brahm, *Macromolecules*, **24**, 1096 (1991). (b) P. Penczek, K. C. Frisch, B. Szczepaniak, and E. Rudnik, *J. Polym. Sci. Polym. Chem.*, **31**, 1211 (1993). (c) M. Tanaka and T. Nakaya, *Makromol. Chem.*, **190**, 3067 (1989).
10. (a) S. W. Kantor and T.-C. Sung, *Macromolecules*, **26**, 3758 (1993). (b) A. B. Conciatori, E. W. Choe, and G. Farrow, U.S. Pat. 4,440,945 (1984) to Celanese Corp.
11. (a) R. A. M. Hikmet, *Adv. Mater.*, **4**, 679 (1992). (b) M. H. Litt, W.-T. Whang, K.-T. Yen, and X.-J. Qian, *J. Polym. Sci. Polym. Chem.*, **31**, 183 (1993). (c) G. Galli, M. Laus, and A. S. Angeloni, *Makromol. Chem.*, **187**, 289 (1986). (d) A. B. Conciatori, E. W. Choe, and G. Farrow, U.S. Pat. 4,452,993 (1984) to Celanese Corp. (e) D. J. Broer, R. G. Gossink, and R. M. Hikmet, *Angew. Makromol. Chem.*, **183**, 45 (1990).
12. J. Makhlof, in *Encyclopedia of Chemical Technology*, H. F. Mark, D. F. Othmer, C. G. Overberger, and G. T. Seaborg, Eds., Wiley, New York, 1983, Vol. 18, pp. 575-594.
13. T. Hunt, in *Developments in Reinforced Plastics*, G. Pritchard, Ed., Applied Science, London, 1980, Vol. 1, pp. 59-86.
14. S. L. Kwolek, P. W. Morgan, and J. R. Schaeffgen, in *Encyclopedia of Polymer Science and Engineering*, H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, Eds., Wiley, New York, 1987, Vol. 9, pp. 1-61.
15. (a) W. R. Krigbaum, H. Hakemi, and R. Kotek, *Macromolecules*, **18**, 965 (1985). (b) R. Sinta, R. A. Minns, R. A. Gaudiana, and H. G. Rogers, *Macromolecules*, **20**, 2374 (1987). (c) H.-W. Schmidt, *Makromol. Chem. Macromol. Symp.*, **26**, 47 (1989). (d) M. Holweg and H.-W. Schmidt, *Makromol. Chem.*, **190**, 1587 (1989). (e) H. R. Kricheldorf and J. Engelhardt, *J. Polym. Sci. Polym. Chem.*, **28**, 2335 (1990).
16. W. Brüggling, U. Kampschulte, H.-W. Schmidt, and W. Heitz, *Makromol. Chem.*, **189**, 2755 (1988).
17. H.-W. Schmidt and D. Guo, *Makromol. Chem.*, **189**, 2029 (1988).

Received July 11, 1994

Accepted October 7, 1994