was fairly uniform in spite of the weakly electron withdrawing effect of the ester group. The reversibility of doping indicated the existence of bromine that was weakly complexed with the thiazyl segment. The PDBPD–TEG polymer having a longer thiazyl segment exhibited a higher doped conductivity, both before and after pumping, as was the case with the model counterparts.[9]

The pristine polymers do not exhibit an electron paramagnetic resonance signal, but on oxidation with Br_2 they exhibit a signal with *g* values ranging from 2.0069 to 2.011. These values compare fairly well with those of the model compounds, indicating that the same kind of radical cation postulated for the model systems[9] are formed in the case of the polymers.

The maximum doped conductivities of the polymers compare fairly well with those of the model systems. However, the doping is significantly more reversible in the case of the polymers. This suggests that the charge transfer in the case of the polymers may be weaker. It is also interesting that in spite of the significant dilution of the conducting segments with insulating spacers in the case of the polymers, their maximum doped conductivity is comparable to that of the model counterparts. This suggests that there is sufficient constructive interaction between the planar phenylthiazyl segments in the polymers to allow charge transport.

Conclusion

Polymers that incorporate (phenylthio)phenyldithiazayl and phenylenedithiobis(phenyldithiazyl) segments along with flexible spacers have been synthesized. Although the PTPD–TEG polymer with a flexible triethylene glycol spacer was soluble and fusible, the PDBPD–TEG polymer was insoluble. This may be due to the stronger interaction between the longer thiazyl segments in the latter. The conducting properties of the model systems and polymers are similar, ranging from 10^{-3} to 10^{-5} $(\Omega\ \mathrm{cm})^{-1}$ upon doping with bromine.

Registry No. **1** (copolymer), 114719-89-0; **1** (SRU), 114719-85-6; **2** (copolymer), 114719-91-4; **2** (SRU), 114719-86-7; **3** (copolymer), 114719-93-6; **3** (SRU), 114719-87-8; **4** (copolymer), 114719-96-9; **4** (SRU), 114718-86-4; C_{10}, 114719-88-9; DEG, 114719-90-3; TEG, 114719-92-5; *p*-(benzylthio)benzoyl chloride, 114719-94-7; *p*-(benzylthio)benzoic acid, 22855-95-4; 1,10-decanediol, 112-47-0; diethylene glycol, 111-46-6; triethylene glycol, 112-27-6; bromine, 7726-95-6.

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[2.2]Paracyclophane End-Capped Polyquinoline Prepolymers: Synthesis, Processing, and Thermal Properties

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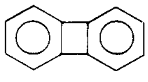
ABSTRACT: Flexible polyquinolines (DP = 11, 22) containing [2.2]paracyclophane end caps were prepared, using 4-acetyl[2.2]paracyclophane as the capping agent. Thermal analysis of the oligomers showed the [2.2]paracyclophane ring-opening exothermic maximum to be near 350 °C. The oligomers were melt-pressed at 350 °C under a 5000-lb load for various times, giving high-quality films which exhibited good Young's moduli. Film quality and moduli were higher for the DP = 22 oligomer. TGA analysis showed the films to be stable to about 550 °C in both air and argon. Oxidative aging at 320 °C for 100 h gave moderate weight losses, relative to various quinoline oligomers end capped with biphenylene.

Introduction

In previous efforts to prepare readily processible polyquinoline prepolymers which, upon curing, would give highly cross-linked, thermally stable polymer networks, biphenylene (1) has been studied as an end-capping agent. Biphenylene end-capped oligomers provided cured films (and composites) possessing thermal stability that was not as good as might have been expected on the basis of a consideration of the types of structures generated by the thermolysis of biphenylene in an aromatic medium.[1,2] Attempts were made to increase the cross-linking densities obtainable from oligomers of a conveniently processible size by incorporation of reactive internal acetylene functionality,[3] which could react with the biphenylene units



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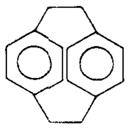

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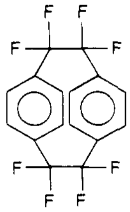

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Table I
Molecular Weights of [2.2]Paracyclophane End-Capped Polyquinoline Prepolymers Determined by Various Methods

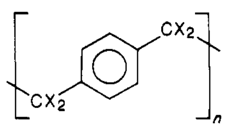
oligomer	$\overline{DP}_n$(calcd)	$\overline{DP}_n$(NMR)	viscosity[a] $\overline{DP}_n$	viscosity[a] $\overline{M}_n$	GPC[b] $\overline{M}_n$	GPC[b] $\overline{M}_w$	GPC[b] $\overline{M}_w/\overline{M}_n$
8a	22	18	19	11 800	32 000	99 000	3.08
8b	11	10	13	8 723	18 000	61 000	3.28

[a] $[\nu] = K\overline{M}_n{}^a$. [b] Relative to polystyrene standards.

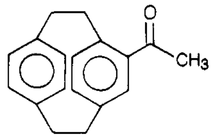
to yield phenanthrene linkages. In cured films from these polymers, Young's moduli above the T_g did increase with increasing content of internal acetylene, indicating improved cross-linking densities. However, the thermooxidative stability of these polymer films was still poor. Consequently, we have sought other end-capping agents that would be useful as alternatives to biphenylene.

Previous applications of functionalized [2.2]paracyclophanes as internal cross-linking agents in aromatic polyethers, polysulfones, polyketones,[4] and polybenzimidazoles[5] brought to our attention the possible utility of the [2.2]paracyclophane system (**2**) for our own work with polyquinolines and polyimides. The ring-opening reaction of the cyclophane system does not give off volatiles. In addition, DSC analysis of the polybenzimidazoles containing internal paracyclophane linkages exhibited cyclophane ring-opening exotherms beginning at 350 °C.[5] This suggested that [2.2]paracyclophane end caps should undergo thermal ring opening in polyquinolines at a much lower temperature than biphenylene, and that consequently a ring-opening catalyst would not be necessary to avoid high curing temperatures.

Incorporation of the octafluorinated [2.2]paracyclophane **3** into poly(ether–sulfone–ketones)[6] served to demonstrate its ability to give better thermal stability to the resulting cross-link sites, presumably due to the greater resistance of its perfluorinated benzylic positions to thermal oxidation. This conclusion is further supported by the favorable comparison of the fluorinated poly-*p*-xylylene **4b** with its parent analogue **4a**.[7]



4a, X=H
b, X=F



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Incorporation of the non-fluorinated end-cap **5** into polyquinolines and polyimides serves as a useful model study, since polymers containing **2** or **3** should cure in a very similar fashion, differing primarily in their thermooxidative stability. In the present work, we report the synthesis, the characterization, and the thermal and mechanical analyses of polyquinoline oligomers end capped with [2.2]paracyclophane.

Results and Discussion

Oligomer Synthesis and Properties. Two oligomeric polyquinolines of DP = 22 and 11 (**8a,b**) were prepared by the acid-catalyzed Friedlander copolymerization of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**6**) and 4,4′-diacetyldiphenyl ether (**7**).[9] The stoichiometric imbalance between the two monomers was controlled in order to obtain the desired degree of polymerization in each case. The bis(amino ketone) monomer **6** was used in excess, allowing the resulting oligomers to be end capped with 4-acetyl[2.2]paracyclophane (**5**).

The number-average molecular weights ($\overline{M}_n$) of oligomers **8** were determined by dilute solution viscosity measurements and gel permeation chromatography (GPC). Other GPC data are also reported (Table I). Dilute solution viscosity measurements in chloroform gave extrapolated intrinsic viscosities that were substituted into the Mark–Houwink equation ($K = 9.0 \times 10^{-4}$ and $a = 0.66$ for polyquinolines, by membrane osmometry[10]) to obtain $\overline{M}_n$ values. GPC data were obtained in chloroform, relative to polystyrene standards, and gave molecular weight values that were significantly higher than was expected or indicated by the other methods. Also, comparison of multiple GPC runs with the same oligomer showed the results to be poorly reproducible. The number-average degree of polymerization ($\overline{DP}_n$) of the oligomers could also be obtained directly, by comparing the ^{1}H NMR integration of the aromatic protons on the polymer chain to that of the aromatic protons on the [2.2]paracyclophane end caps (assuming complete end capping).

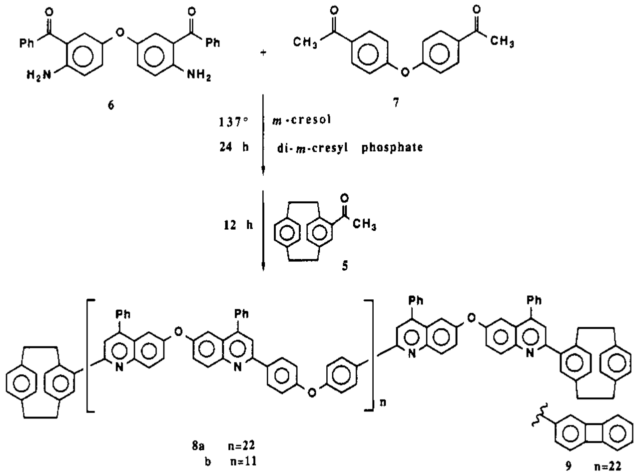

Figure 1. Preparation of [2.2]paracyclophane end-capped oligomeric quinolines (**8**).

Table II
Differential Scanning Calorimetry of Uncured Oligomers 8

oligomer	T_g, °C	exo$_{max}$, °C	T_d,[a] °C
8a	252	357	490
8a[b]	259	...	485
8b	252	352	470
8b[c]	...	352	490
9	238	*d*	400

[a] Onset of decomposition under argon. [b] Cured for 30 min at 350 °C in the sample cup, then allowed to cool, and reanalyzed as usual. [c] Heated isothermally for 1 h at 270 °C and then heated as usual. [d] Not visible; occurs above onset of decomposition.

The thermal properties of the uncured oligomers are shown in Table II. The properties of an analogous biphenylene end-capped oligomer (DP = 22) (**9**), prepared previously,[3] are included for comparison. The T_g's of oligomers **8** are somewhat higher than that of biphenylene end-capped oligomer **9**. The cyclophane ring-opening exotherm can be observed to be at a maximum just above 350 °C, indicating that this temperature should suffice for effective curing of the oligomers, without the need for a ring-opening catalyst. This was shown to be the case by

Table III
Differential Scanning Calorimetry of Melt-Pressed Films Prepared from Oligomers 8

oligomer	cure conditns[a]	T_g, °C	T_d,[b] °C
8a	*c*	252	490
	30 min	258	485
	1 h	258	485
	2 h	255	490
8b	*c*	252	470
	30 min	254	470
	2 h	250	463
	d	251	450
9	*c*	238	400
	2 h	247	368

[a] 350 °C under a load of 5000-lb in air, unless otherwise noted. [b] Onset of decomposition under argon. [c] Uncured powder sample. [d] 270 °C for 1 h, followed by 350 °C for 30 min.

an experiment in which the DP = 22 oligomer **8a** was cured in the DSC sample cup at 350 °C for 30 min under argon. Reanalysis of the same sample then showed a slight increase in T_g, as well as the complete absence of the initially large ring-opening exotherm.

Another DSC experiment was carried out, where a sample of **8b** was heated isothermally at 270 °C (above the T_g) for 1 h, before continuing the temperature increase. The resulting ring-opening exotherm still exhibited 95% of the area (in cal/g) that was observed for a sample of **8b** analyzed normally, indicating that the oligomer can be processed above its T_g without curing and then heated to complete the cure. A cured film was prepared in the same fashion (vide infra).

Oligomer Processing and Cured Properties. Oligomers **8** were melt-pressed at 350 °C under a 5000-lb load for varying times. The resulting dark amber films were of good quality and did not contain the large voids that are characteristic of films similarly prepared from biphenylene end-capped oligomers. Oligomer **8b** gave films that were slightly inferior to those from **8a**, exhibiting less elasticity and showing small voids around the edges of the pressed films. A previously prepared[3] biphenylene end-capped oligomer (DP = 22) (**9**) was cured under the same conditions, so that its properties could be compared to those of films from **8a** and **8b**.

DSC analyses were carried out on the cured films (Table III). Data for the uncured oligomers are again shown for comparison. A slight increase in the T_g was observed upon curing the DP = 22 oligomer **8a**, but the DP = 11 oligomer **8b** showed little change in the T_g. The third film made from **8b** was cured at 270 °C for 1 h and then at 350 °C for 30 min. These conditions were expected to give a more uniform film by allowing the sample to flow better, above its T_g, before the temperature was raised to bring about cross-linking. However, the resulting film was essentially identical with the other two films from **8b** and showed similar properties. The cured film from **9** showed voids and the expected T_g. The onset of decomposition (T_d) of **9** under argon (by DSC) occurred at a much lower temperature than that for films from **8a** and **8b**.

The film from **8a** that was cured for 30 min showed no solubility in chloroform, methanesulfonic acid, trifluoromethanesulfonic acid, or concentrated sulfuric acid after 3 days. The sample in concentrated sulfuric acid did swell, soften, and lose its elasticity, however.

Dynamic mechanical analysis (DMA) showed T_g's very close to those obtained from the DSC. Young's moduli of films from **8a** (Table IV) indicated good mechanical properties and were fully consistent with values obtained for previous films from biphenylene end-capped oligomers.[9] Young's moduli of films from **8b** were slightly lower. These films had slightly mottled surfaces, appearing to have contracted slightly during the curing process (or upon cooling). Thus, the measured film thicknesses could be larger than the actual average thicknesses, giving lower calculated Young's moduli. The film prepared from **9** showed lower moduli, roughly confirming previous results for thermally cured films of the same composition.[3]

Table IV
Dynamic Mechanical Analysis of Melt-Pressed Films from Oligomers 8

oligomer	cure conditns[a]	E''_{max}, °C	$E'_{50\,°C}$, dyn/cm^2	$E'_{300\,°C}$, dyn/cm^2
8a	30 min	261	2.68×10^{10}	1.92×10^{8}
	1 h	261	2.93×10^{10}	1.67×10^{8}
	2 h	252	2.90×10^{10}	1.22×10^{8}
8b	30 min	250	2.21×10^{10}	1.29×10^{8}
	2 h	251	2.23×10^{10}	1.06×10^{8}
	b	253	2.55×10^{10}	1.15×10^{8}
9	2 h	271	1.24×10^{10}	6.20×10^{7}

[a] 350 °C under a load of 5000-lb in air, unless otherwise noted. [b] 270 °C for 1 h, followed by 350 °C for 30 min.

Table V
Isothermal Aging of Melt-Pressed Films from Oligomers 8 for 100 h at 320 °C in Air[a]

oligomer	cure conditns[b]	weight loss, %
8a	30 min	11.9
	1 h	10.1
	2 h	23.9
8b	30 min	21.3
	2 h	25.8
	c	21.1
9	2 h	8.1[d]

[a] Circulating-air oven. [b] 350 °C under a load of 5000-lb in air, unless otherwise noted. [c] 270 °C for 1 h, followed by 350 °C for 30 min. [d] Average of two samples.

Samples of the several cured films were thermooxidatively aged in circulating air at 320 °C for 100 h (Table V). Weight losses from oligomers **8** were somewhat greater than that previously reported for the biphenylene end-capped oligomer (DP = 22) cured in the presence of a nickel catalyst.[9] However, a similar biphenylene-capped film cured thermally (without catalyst) showed a much greater weight loss than films from **8** (greater than 75% at 25 h),[3] as did films prepared from oligomers with internal acetylene linkages[3] or pendent biphenylene groups[2] (up to 88% at 100 h). However, the film from **9** showed less weight loss than the films from oligomers **8**, which is quite incongruous with previous studies. The film prepared from **9** was twice as thick as previously used films,[2,3,9] showing the results of isothermal oxidation to be highly dependent on the method of sample preparation (i.e., sample geometry).

The short-term thermal stability of the six cured films was examined by thermal gravimetric analysis (TGA) (Table VI). All films exhibited good thermal stability to above 500 °C in both argon and air, with the maximum rate of weight loss ("break") occurring around 570 °C for all samples. The uncured powder and cured films from **8b** were close in stability, although the uncured powder was somewhat slower to lose weight. The stability of **8a** increased with increasing cure time, showing the highest stability in the film cured for 1 h. The onset and weight loss temperatures for both biphenylene end-capped **9** and the corresponding cured film were quite comparable, showing little dependence of stability on whether melt processing had been carried out. All samples demonstrated stability in air comparable to and sometimes greater than that in argon.

Table VI
Thermal Gravimetric Analysis of Oligomers 8 and Melt-Pressed Films Prepared from Them

		argon, °C			air, °C		
oligomer	cure conditns[a]	onset	5% loss	20% loss	onset	5% loss	20% loss
8a	[b]	534	518	550	529	522	554
	30 min	535	546	572	543	547	593
	1 h	553	564	624	555	564	622
	2 h	547	556	620	546	553	608
8b	[b]	552	563	645	556	569	638
	30 min	549	553	607	549	557	603
	2 h	527	556	546	545	553	607
	[c]	547	556	614	546	553	600
9	[b]	568	577	614	571	583	657
	2 h	557	566	610	558	576	642

[a] 350 °C under a load of 5000-lb in air, unless otherwise noted. [b] Uncured powder sample. [c] 270 °C for 1 h, followed by 350 °C for 30 min.

Conclusions

Polyquinoline prepolymers end capped with [2.2]paracyclophane undergo effective curing at 350 °C without the need for a ring-opening catalyst, giving good quality, insoluble films. The cured films exhibit good thermal properties and Young's moduli, comparable to those obtained in films from catalytically cured biphenylene end-capped oligomers. TGA and isothermal aging studies show that films prepared from cyclophane end-capped oligomers are somewhat less thermally stable than those similarly prepared from biphenylene end-capped oligomers.

Experimental Section

The monomers 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (6)[10] and 4,4′-diacetyldiphenyl ether (7)[11] and the catalyst di-*m*-cresyl phosphate[12] were prepared and purified according to the published procedures.

Intrinsic viscosity measurements on polymer solutions in chloroform were obtained with a No. 50 Cannon-Ubbelohde microdilution viscometer.

Gel permeation chromatography was carried out by using chloroform at a flow rate of 2.5 mL/min with a Waters GPC equipped with a 6000-A pump, U6K injector, R 401 RI detector, 730 data module, and a 500-Å μ-Styragel column.

Thermal and mechanical analyses of the oligomers and melt-pressed films were carried out by using a Du Pont 9900 thermal analyzer with a Du Pont 910 differential scanning calorimeter (heating rate 20 °C/min), a Du Pont 951 thermogravimetric analyzer (heating rate 10 °C/min), and a Du Pont 983 dynamic mechanical analyzer (heating rate 5 °C/min, horizontal clamps, resonant mode). Data from the dynamic mechanical analyzer was shown to correlate well with that obtained from a Rheovibron DDV-II-C dynamic viscoelastometer, by reanalysis of several film samples prepared in previous work. Isothermal aging studies were carried out on 25–70-mg film samples, which were placed in weighed vials, covered with watch glasses, and allowed to age in a 320 °C gas chromatograph oven in an atmosphere of circulating air.

4-Acetyl[2.2]paracyclophane (5). Following the published procedure,[13] 1.24 g (9.30 mmol) of aluminum chloride was placed in a flame-dried 100-mL flask equipped with a stir bar. The flask was purged with dry nitrogen. To the flask were then added by syringe 55 mL of dichloromethane (distilled from P_2O_5) and 3.7 mL (4.1 g, 52 mmol) of acetyl chloride (freshly distilled). The mixture was cooled to −30 °C, and 4.963 g (23.83 mmol) of [2.2]paracyclophane was rapidly added with stirring. The temperature was maintained at −25 °C for 15 min and then cooled to −40 °C. The cold mixture was poured carefully into cold, dilute HCl. The mixture was allowed to warm to room temperature and partitioned between chloroform and water. The aqueous phase was extracted with fresh chloroform, and the organics were combined and washed twice with water and once each with saturated aqueous sodium bicarbonate, water, and saturated aqueous NaCl. The solution was dried over $MgSO_4$ and filtered. The chloroform was removed under reduced pressure to give a yellow oil. Recrystallization from 95% ethanol, followed by recrystallization from ethyl acetate/hexanes gave white crystals. An ethyl acetate solution of the product was purified by medium-pressure liquid chromatography (MPLC) on silica gel, eluting with 9:1 hexanes/ethyl acetate. Removal of the solvent under reduced pressure and another recrystallization from ethyl acetate/hexanes gave in two crops 1.9120 g (32%) of white crystalline product: mp 111.8–112.3 °C, uncorr. (lit.[13b] 109.7–110.4 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.92 (d, 1), 6.51 (m, 6), 3.97 (m, 1), 3.12 (m, 6), 2.84 (m, 1), 2.46 (s, 3).

[2.2]Paracyclophane End-Capped Polyquinoline 8a. Into the bottom of a resin kettle equipped with a nitrogen inlet, a mechanical stirrer, and a nitrogen outlet were placed 22.5 g of di-*m*-cresyl phosphate, 3.8 g of distilled *m*-cresol, 1.3164 g (3.2229 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (6), and 0.7628 g (2.9998 mmol) of 4,4′-diacetyldiphenyl ether (7). The kettle was flushed with nitrogen for about 30 min with stirring and was then placed in an oil bath preheated to 138 °C. Stirring was continued for 28 h under an atmosphere of static nitrogen. Stirring and heating were halted while 0.2321 g (0.9234 mmol) of 4-acetyl[2.2]paracyclophane (5) was added to the mixture. Stirring and heating were continued for 15 h. The hot, viscous mixture was poured slowly into a stirred solution of 450 mL of ethanol and 50 mL of triethylamine. The resulting mixture was stirred for 1 h, chopped in a Waring blender (on low setting for 30 s, then on high for 45 s), and filtered. The solid polymer was continuously extracted for 19 h with ethanol containing 10% v/v triethylamine, air-dried, and then dried at 110 °C under reduced pressure for 8 h. The polymer was redissolved in 90 mL of chloroform and reprecipitated by slow addition to a stirred solution of 900 mL of ethanol and 100 mL of triethylamine. The polymer was collected by filtration and dried as before.

[2.2]Paracyclophane End-Capped Polyquinoline 8b. The above procedure was followed except that 1.4434 g (3.5337 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (6), 0.7628 g (2.9998 mmol) of 4,4′-diacetyldiphenyl ether (7), 22.5 g of di-*m*-cresyl phosphate, 3.8 g of *m*-cresol, and 0.4743 g (1.887 mmol) of 4-acetyl[2.2]paracyclophane (5) were used.

Neat Resin Melt Processing. A Wabash hydraulic press (Model 1210) that had been fitted with Carver heat platens was used for melt processing. The platens were heated to 350 °C while the polymer sample was prepared: A 200-mg powder sample of the polymer was placed in a small pile between two copper sheets (0.010 in. thick). Two L-shaped pieces of copper sheet were used as spacers surrounding the sample. The assembly was placed between the preheated platens and melt processed at 350 °C under a 5000-lb load for the desired amount of time. The platens were allowed to cool to 200 °C without releasing the pressure, whereupon the sample assembly was removed from the press and quickly plunged into tap water. The copper sheets were carefully peeled away from the cured film, which was swirled in concentrated aqueous ammonia for 30 min, thoroughly rinsed with water, and air-dried.

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Registry No. 8, 114583-84-5.

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Rheology of a Twin Liquid Crystalline Polymer

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ABSTRACT: Phase transitions of a twin liquid crystalline polymer (TLCP), which was synthesized from 4-[(4′-alkoxybenzoyl)oxy]benzoyl chloride and α,ω-dihydroxy-telechelic polytetrahydrofuran, have been determined by measurements of linear viscoelastic properties. In the phase-separated mesophase state, the TLCP displayed high elasticity to small-amplitude deformation, due to mesogen-induced physical cross-linking. As the strain amplitude increased, shear thinning affected both dynamic and steady flow properties. This effect is assumed to be due to a reduction of tie molecules and an increase of loops in the physical network. If the average shear rate of oscillatory flow was defined as $\bar{\dot{\gamma}}_d = 4\gamma_0\omega/2\pi$, a good agreement of $\eta^*(\bar{\dot{\gamma}}_d) \approx \eta(\dot{\gamma})$ was found in the shear thinning region and the high shear rate plateau. After shear thinning a TLCP, structural recovery took several days, unless the sample was temporarily heated to the isotropic state. However, above the clearing temperature of about 65 °C, the polymer became single phased and showed rheological behavior typical for a polymeric melt of low molecular weight.

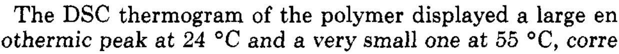
Introduction

Polymers in the liquid crystalline state form anisotropic textures due to the interaction of the mesogenic groups.[1–8] As a result, the basic flow units are not only molecular chains, but also macrostructural units in which a large number of molecular chains move cooperatively. This gives rise to unusual rheological phenomena, including long relaxation time,[3,9–12] elasticity,[3,12–14] and distinct shear thinning effect at low shear rates.[1–6,11,14,15] It is apparent that the study of the rheology of liquid crystalline polymers is still in its infancy and much more research in a wide variety of liquid crystalline polymers is needed to improve our understanding in this field.

A twin liquid crystalline polymer (TLCP)[16] consists of a flexible center chain with mesogenic segments on both ends. Below the clearing temperature (about 65 °C for this TLCP), mesogenic ends form a separated nematic phase. In the present work, rheology of a TLCP was studied in both the microphase-separated state and the compatible isotropic state, using dynamic as well as steady flow measurements. The experimental observations are related to physical cross-linking through phase-separated mesogen domains.

Experimental Section

Materials. The TLCP studied in this work was synthesized from 4-[(4′-alkoxybenzoyl)oxy]benzoyl chloride[16] and α,ω-dihydroxy-telechelic polytetrahydrofuran of 2000 M_w, having the following structure as determined by NMR:



$$CH_3CH_2CH_2CH_2O\text{–}◎\text{–}\overset{O}{\overset{\|}{C}}\text{–}O\text{–}◎\text{–}\overset{O}{\overset{\|}{C}}\text{–}O(CH_2CH_2CH_2CH_2O)_{28}\text{–}\overset{O}{\overset{\|}{C}}\text{–}◎\text{–}O\text{–}\overset{O}{\overset{\|}{C}}\text{–}◎\text{–}OCH_2CH_2CH_2CH_3$$

The DSC thermogram of the polymer displayed a large endothermic peak at 24 °C and a very small one at 55 °C, corresponding to the phase transitions of crystal to liquid crystal and liquid crystal to isotropic, respectively. The enthalpies and entropies of these transitions have been reported.[16] Under the polarizing microscope, dispersed liquid crystalline domains were observed in the temperature range 24–55 °C, but they completely disappeared above 65 °C.

Apparatus. Dynamic and steady shear flow measurements were performed on a Rheometrics dynamic spectrometer (RDS) and a Rheometrics stress rheometer (RSR), respectively, using the cone/plate geometry. Samples were molded in the rheometers at 75 °C. On RDS, in addition to linear viscoelastic properties, we measured the apparent storage modulus G'_a, loss modulus G''_a, and complex viscosity η^*_a at large strain amplitude beyond the linear viscoelastic region.

Phase Transitions. Figure 1a shows the storage modulus G' and the loss modulus G'' of the TLCP, measured at a frequency of 10 rad/s and in the linear viscoelastic region, as a function of temperature. From 20 to 32 °C, the moduli G' and G'' decayed by 2 orders of magnitude, due to the transition of the crystalline state to a mesophase state. In the mesophase state, G' was still higher than G'', and both moduli decreased gradually with increasing temperature. The transition from the mesophase state to the isotropic state started at 45 °C and completed at about 65 °C, accompanied by 10^3- and 10^2-fold decrease in G' and G'', respectively. These phase-transition temperatures as measured with linear viscoelastic properties are in good agreement with those determined by DSC and polarizing microscopy.[16] By comparison, α,ω-dihydroxy-telechelic polytetrahydrofuran did not display a mesophase state by itself. Above the melting temperature at 30 °C, both moduli G' and G'' decreased regularly as the temperature increased (Figure 1b).

In the present work, the rheology of this TLCP is characterized at 45 °C (liquid crystalline state), 55 °C (middle point of the transition zone), and 65 °C (isotropic state).

Linear viscoelastic properties of the TLCP at the three temperatures are shown in Figure 2. At 45 °C, the polymer melt exhibited a high storage modulus G', almost like an elastomer. At 65 °C, G' was much lower than G'' in the experimental frequency range, i.e., the polymer melt was essentially characterized

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