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NEW POLYMER SYNTHESES. 89. THERMOSETTING CHOLESTERIC OLIGOESTERS HAVING PROPARGYL ENDGROUPS

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ABSTRACT

Three series of cholesteric oligoesters containing propargyl endgroups were prepared by polycondensations of three different dicarboxylic acid dichlorides with mixtures of diols and monofunctional propargyl derivatives in pyridine. These three series are based on terephthaloylchloride, naphthalene-2,6-dicarbonylchloride, and biphenyl-4,4′-dicarbonylchloride. *tert*-Butylhydroquinone, phenylhydroquinone, and isosorbide were the diols, and propargyl alcohol, 4-propargylthiophenol, and 6-propargyloxynaphthaloyl chloride served as chain stoppers. All isolated oligoesters were thermotropic, but only a few of them were capable of forming a Grandjean texture upon shearing of the cholesteric melt. The thermal crosslinking of the propargyl endgroups was monitored by an exothermic process in the DSC measurements. The lowest cure temperatures (200–240°C) were observed for the 6-propargyloxy-2-naphthoic acid endgroups. Thermal crosslinking in the cholesteric phase was observed for four samples.

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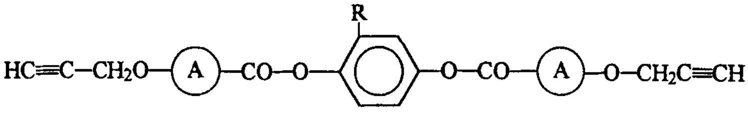
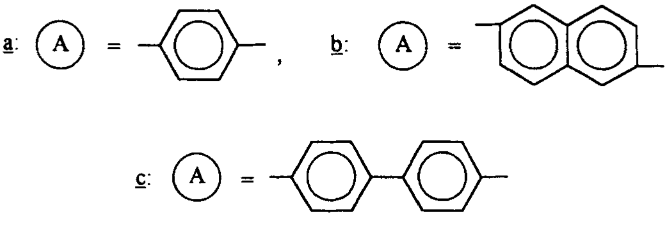
INTRODUCTION

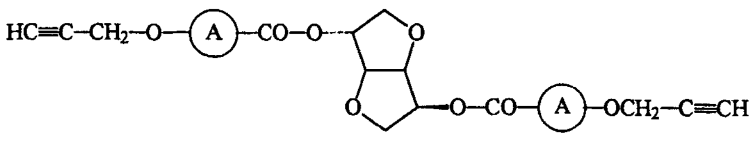
Cholesteric oligomers or polymers which are capable of forming a stable Grandjean (GJ) texture in the melt are of potential interest as colored films, lacquers, and pigments [1]. The GJ texture [2, 3] is a macroscopic alignment of the cholesteric domains containing helical supermolecular arrays of mesogens. Provided the pitch of these helices matches the wavelengths of visible light, a narrow band of circularly polarized light is reflected, but no light is absorbed. However, any application of these interesting optical properties requires a fixation of the GJ texture formed in the melt. One strategy designed for the fixation of a GJ texture consists of the preparation of thermosetting cholesteric oligomers bearing thermolabile endgroups. Acetylene groups play a prominent role among the few functional endgroups suited for thermal cure [4–6].

Propargyl endgroups do not possess outstanding thermostability or thermolability, but they are useful for a thermal cure process, and they are easy and inexpensive to introduce. In a recent paper [7] we reported on crystalline diesters of structure **1**, which are nematic over a broad temperature range. Upon doping with the chiral diesters **2**, cholesteric melts were obtained which in most cases can form GJ textures, and in a few cases thermal fixation of the GJ texture was feasible. The present work was designed to explore a complementary approach. The chiral isosorbide should be covalently incorporated into oligoesters terminated by propargyl endgroups. In contrast to the diesters 1 these oligoesters will not have an exactly



1a-c





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defined sequence and molecular weight, but they are cooligomers with a broader molecular weights distribution. More positive consequences of their different structure are a lower volatility and a higher melt viscosity than the diesters **1**.

EXPERIMENTAL

Materials

Terephthaloylchloride, 4-toluolsulfonylchloride, and thionylchloride were gifts of Bayer AG (Leverkusen, Germany) and were used as received. Naphthalene-2,6-dicarboxylic acid, biphenyl-4,4′-dicarboxylic acid, 4-mercaptophenol, and propargyl alcohol were purchased from Aldrich Co. (Milwaukee, WI, USA). The acid chlorides were prepared in refluxing thionylchloride. The synthesis of 6-propargyloxy napthyhoyl chloride (mp 118–120°C) was conducted as described previously [6]. Pyridine was distilled over KOH and CaH_2 before use.

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Oligomerizations

I. With X or Y as Chain Stoppers

A concentrated solution of terephthaloyl chloride (8 mmol) in dry chloroform was added dropwise with stirring to a solution of phenylhydroquinone (2 mmol), isosorbide (1 mmol), and 4-propargylthiophenol (2 mmol) in dry pyridine (20 mL) under cooling with ice. Afterward the reaction mixture was stirred for 20 hours at 20–25°C and finally refluxed for 2 hours. The reaction mixture was then concentrated in vacuo and precipitated into cold methanol. The precipitated oligoester was isolated by filtration, washed with cold methanol, and dried at 65°C in vacuo. Other syntheses were conducted analogously.

II. With Z as Chain Stopper

A concentrated solution of biphenyl-4,4′-dicarbonylchloride (6 mmol) and 6-propargyloxy-2-naphthoylchloride (4 mmol) in dry chloroform was added dropwise with stirring to a solution of phenylhydroquinone (6 mmol) and isosorbide (2 mmol) in dry pyridine (20 mmol) and reacted as described above.

4-Propargylthiophenol

4-Hydroxythiophenol (0.15 mol) was dissolved in 50 mL of 4 N sodium hydroxide (deoxygenated with N_2), propargyltosylate (0.15 mol) was added, and the reaction mixture was refluxed for 2 hours. Afterward the reaction mixture was stirred for 20 hours at 25°C and acidified with 5 N hydrochloric acid to pH 1. The product was extracted with three 150 mL portions of diethyl ether which were combined and dried with Na_2SO_4. Finally, the product was isolated by distillation over a short-path apparatus at a bath temperature of 180–200°C in a vacuum of 0.01 mbar. Yield 24%.

Analyses. Calculated for C_9H_8OS (164.2): C 65.82%, H 4.91%, S 19.53%. Found: C 65.33%, H 4.90%, S 18.68%.

^{1}H NMR ($CDCl_3$/TMS): δ = 2.32 (s, 1H), 3.37 (s, 2H), 4.70 (s, OH), 6.74 (m, 2H), 7.25 (m, 2H) ppm.

Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20°C.

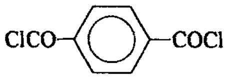
The IR spectra were recorded from KBr pellets with a Nicolet SXB-20 FT-IR spectrometer.

The 100 MHZ ^{1}H-NMR spectra were recorded with a Bruker AC-100 FT-NMR spectrometer in 5 mm o.d. sample tubes.

The DSC measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen.

RESULTS AND DISCUSSION

All oligoesters of this work were prepared from combinations of the monomers A, B, C and I, V, W with addition of the chain stoppers X, Y, or Z. The molar ratios of these combinations and the results are summarized in the Tables 1, 2, and 3. Initially, two synthetic procedures were studied and compared. Procedure I was characterized by the reaction of A, B, or C with mixtures of the diols and chain stoppers in 1-chloronaphthalene at 230°C. No HCl acceptor was added, and the liberated HCl was removed with a slow stream of N_2. Several products obtained by this procedure were partially crosslinked. Therefore, all oligoesters listed in Tables 1-3 were prepared via the second procedure. Procedure II is characterized by



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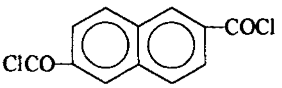

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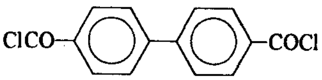

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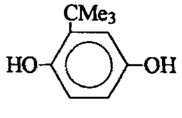

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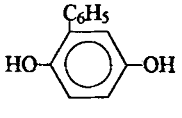

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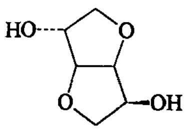
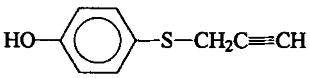


I

$HO-CH_2-C\equiv CH$

X



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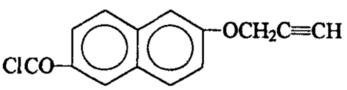

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TABLE 1. Yields and Properties of Propargyl-Group-Terminated Oligoesters Derived from Terephthalic Acid

Polymer	Molar feed ratio	Yield, %	η_{inh},[a] dL/g	T_m,[b] °C	T_{cr},[b,c] °C	T_i,[d] °C	Texture
1	4B + 2V + 1I + 2Y	22	0.07	69	246	180–185	Homeotropic
2	4B + 2W + 1I + 2Y	73	0.07	117	248	125–130	Schlieren (T_i ~ 125°C)
3	3B + 3V + 1I + 2Z	4	–	151	242	155–160	Homeotropic
4	3B + 3W + 1I + 2Z	1	–	109	244	180–187	GJ blue (T_i ~ 190°C)

[a] Measured at 20°C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1).

[b] DSC measurements with a heating rate of 20°C/min.

[c] Exotherm of the crosslinking process.

[d] From optical microscopy with a heating rate of 10°C/min.

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the reaction of the dicarboxylic acid dichlorides (A, B, C) with the diols and chain stoppers in pyridine at low temperatures. All oligoesters prepared in this way were completely soluble in organic solvents. The chemical structures of the isolated oligoesters were characterized by IR- and ^{1}H-NMR spectroscopy. The IR spectrum of Fig. 1 is a typical example for all oligoesters of this work. It exhibits the strong band of the ester CO stretch vibration at 1730 cm^{-1}, the band of the acetylenic C—H stretch vibration at 3270 cm^{-1}, and the C≡C stretch vibration at 2123 cm^{-1}.

The ^{1}H-NMR spectra of all oligoesters display the typical signals of the propargyl groups (Fig. 2). The doublet signal of the CH_2 group varies with the nature of the attached heteroatom. When bound to an oxygen, the CH_2 protons absorb around 4.4 ppm (Fig. 2A); when attached to a sulfur, the signal appears around 3.8

TABLE 2. Yields and Properties of Propargyl-Group-Terminated Oligoesters Derived from Napthalene-2,6-dicarboxylic

Polymer	Molar feed ratio	Yield, %	η_{inh},[a] dL/g	T_g,[b] °C	T_{cr},[b,c] °C	T_i,[d] °C	Texture
1	4B + 2.0W + 1.0I + 2X	18	0.07	124	290	220–235	GJ bluish
2[e]	4B + 2.0W + 1.0I + 2X	12	0.07	121	314	190–205	GJ bluish
3	4B + 2.5W + 0.5I + 2Y	11	0.05	82	260	95–105	Schlieren
4	4B + 2.0W + 1.0I + 2Y	21	0.08	119	262	205–215	GJ bluish
5	3B + 3.5W + 0.5I + 2Z	32	0.05	190	248	>350	GJ blue
6	3B + 3.0W + 1.0I + 2Z	31	0.09	113	242	205–220	GJ bluish

[a] Measured at 20°C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1).

[b] From DSC measurements with a heating rate of 20°C/min.

[c] Exotherm of the crosslinking process.

[d] From optical microscopy with a heating rate of 10°C/min.

[e] A 1:1 mixture of pyridine; 1,4-dioxane was used as the reaction medium.

TABLE 3. Yields and Properties of Propargyl-Group-Terminated Oligoesters Derived from Biphenyl-4,4′-dicarboxylic acid

Polymer	Molar feed ratio	Yield, %	η_{inh},[a] dL/g	T_m,[b] °C	T_{cr},[c] °C	T_i,[d] °C	Texture
1	4C + 2.0W + 1.0I + 2X	31	0.09	124	300	>450[e]	GJ yellow, orange
2	4C + 2.5W + 0.5I + 2Y	36	0.06	94	246	220–225	GJ bluish
3	4C + 2.0W + 1.0I + 2Y	23	0.10	116	247	>450[e]	GJ yellow
4	3C + 3.5W + 0.5I + 2Z	19	0.06	169	248	390–405[e]	Schlieren
5	3C + 3.0W + 1.0I + 2Z	47	0.10	111	237	300–315	GJ yellow

[a] Measured at 20°C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1).
[b] From DSC measurements with a heating rate of 20°C/min.
[c] Exotherm of the crosslinking process.
[d] From optical microscopy with a heating rate of 10°C/min.
[e] Beginning of decomposition at ~350°C.

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ppm (Fig. 2B). Elemental analyses were not performed because the molecular weight and the composition of the oligoesters depend to some extent on the fractionation resulting from the precipitation into methanol.

Further characterization of the isolated oligoesters proved that the syntheses conducted with terephthaloyl chloride (A, see Table 1) were not successful. Two experiments (Nos. 3 and 4) gave extremely low yields, and those oligoesters isolated in higher yields (Nos. 1 and 2, Table 1) did not form a GJ texture.

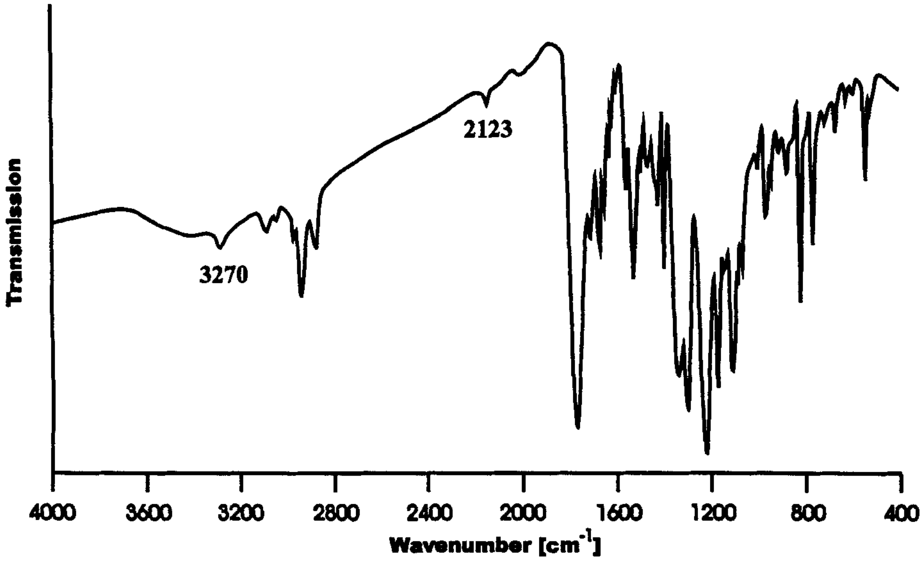

FIG. 1. IR spectrum (KBr pellet) of oligoester No. 6, Table 2.

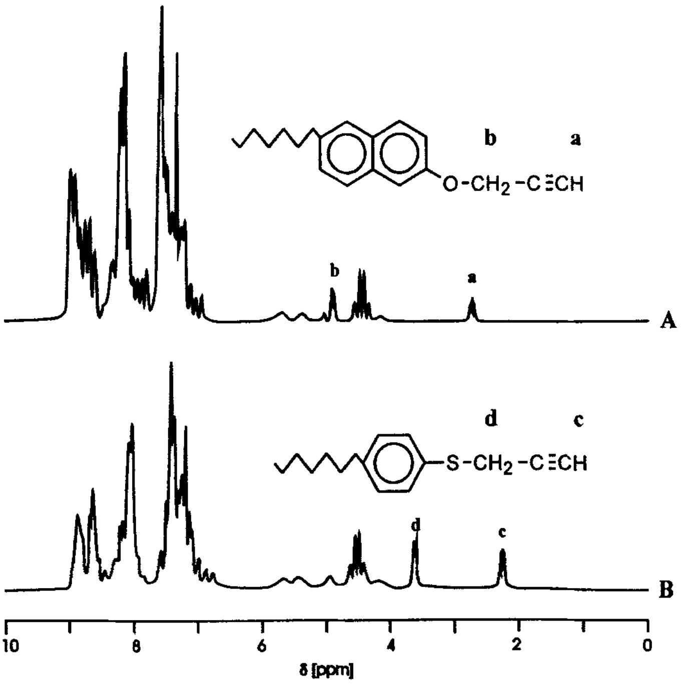

FIG. 2. 100 MHz ^{1}H-NMR spectra recorded from $CDCl_3$/trifluoroacetic acid solutions of (A) oligoester No. 5, Table 2; (B) oligoester No. 4, Table 2.

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The oligoesters derived from naphthalene-2,6-dicarboxyclic acid showed more promising properties (Table 2). Schlieren textures without any tendency to form a GJ texture were observed for the oligoesters Nos. 1-3 (Table 2). Furthermore, relatively low isotropization temperatures (T_I) were found. Interestingly, GJ textures were obtained in five cases upon shearing of the cholesteric melts which originally showed colorful schlieren textures. Unfortunately, the isotropization temperatures of oligoesters Nos. 1, 2, 4, and 6 were considerably lower than the crosslinking temperature T_{cr}, so that a cure of the cholesteric melt was not feasible. However, the oligoester No. 5 (Table 2) yielded blue GJ textures which were stable up to temperatures above 250°C so that the cure produced a fixation of these GJ textures. An interesting result of this investigation is the finding that the cure temperature (T_{cr}) depends very much on the chemical neighborhood of the propargyl group. As illustrated by the DSC curves of Fig. 3, the propargyl ester endgroups require T_{cr}'s around 300°C, the propargylthiophenyl group a T_{cr} around 260°C, and the propargyloxynaphthyl group a T_{cr} around 240°C. It has already been demonstrated in a previous publication dealing with the diesters **1a–c** that the propargyloxy group attached to a naphthalene system is particularly prone to thermal crosslinking. Thus the results of the present study yield the following order of increasing cure temperatures: Z < Y < X.

The characterization of the oligoesters based on biphenyl-4,4′-dicarboxylic acid (Table 3) again provided attractive results. Most oligoesters, with the exception of No. 4, were capable of forming a stable GJ texture upon shearing of the choles-

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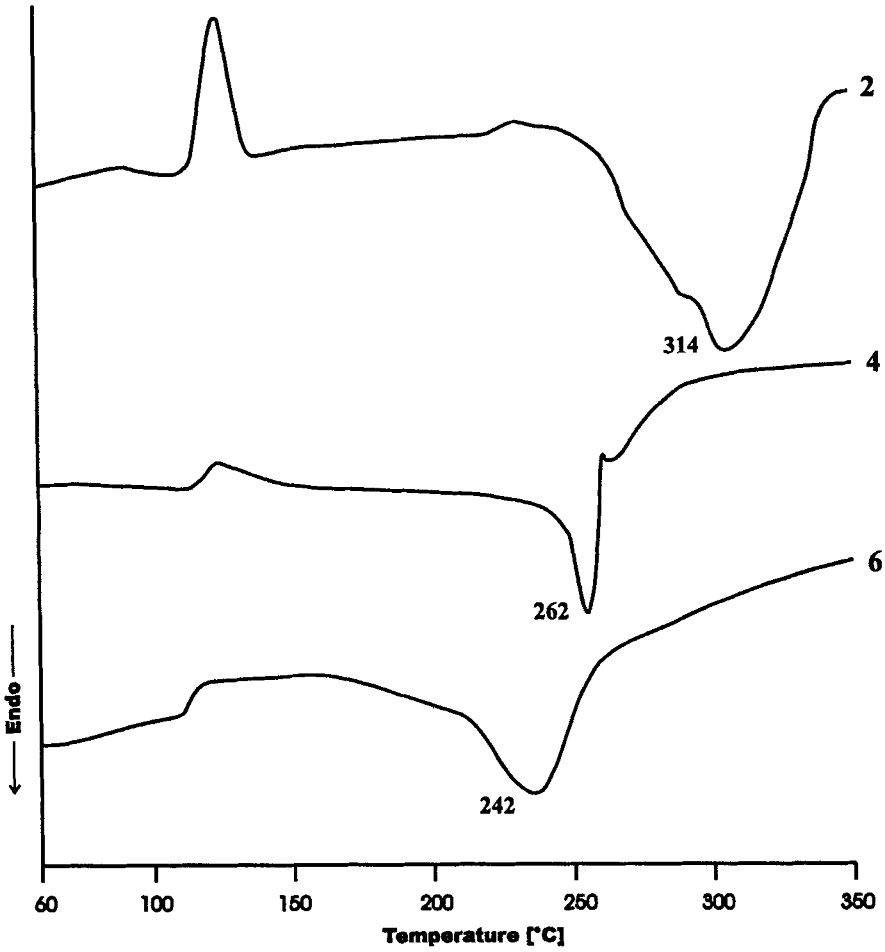

FIG. 3. DSC heating curves (1st heating, 20°C/min) of oligoester No. 2, Table 2; No. 4, Table 2; No. 6, Table 2.

teric melt. Particularly noteworthy is the bright yellow color observed for the GJ textures of the oligoesters Nos. 1, 3, and 5. Most cholesteric polymers we have studied thus far form a blue or bluish GJ texture, and red or yellow colors are relatively rare.

Whereas in the case of oligoester No. 2 the crosslinking occurred in the isotropic melt, the oligoesters Nos. 1, 3-5 (Table 3) allowed crosslinking in the LC phase. In other words, the yellow color of oligoesters Nos. 3 and 5 was fixed by annealing at 230°C for 10-15 minutes. Thus, these oligoesters meet the requirements of thermosetting lacquers or pigments. The properties of all oligoesters listed in Table 3 also confirm the aforementioned order of the reactivity of the propargyl endgroups as illustrated by the DSC measurements presented in Fig. 4.

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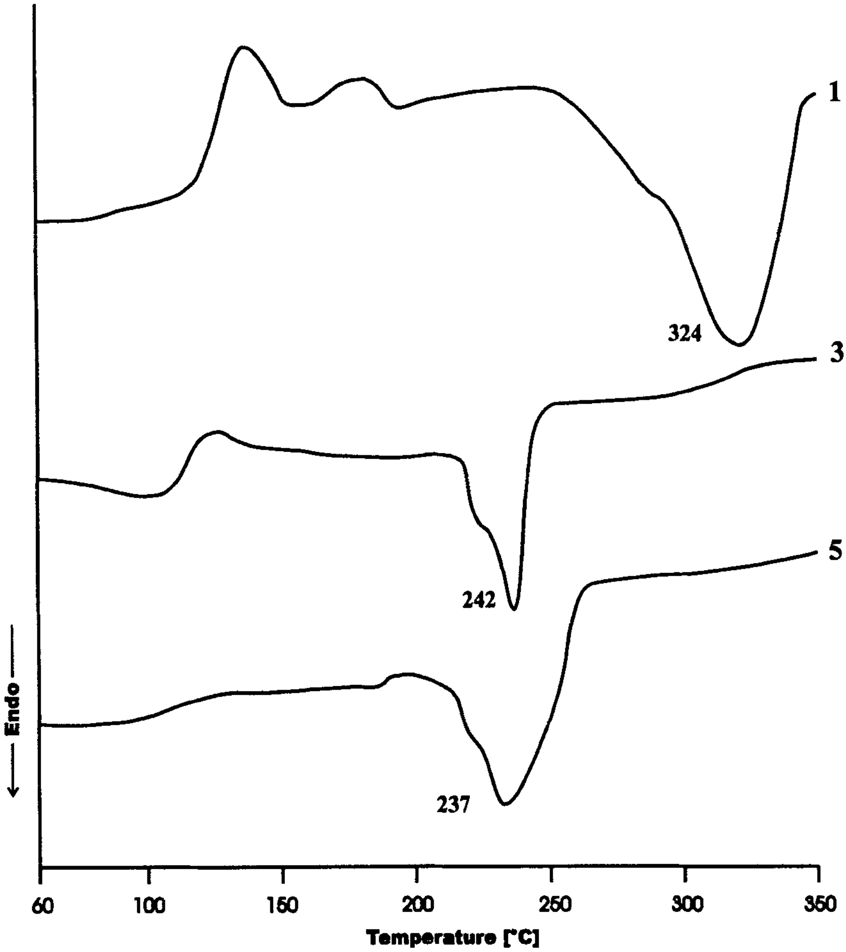

FIG. 4. DSC heating curves (1st heating, 20°C/min) of oligoester No. 1, Table 3; No. 3, Table 3; No. 5, Table 3.

CONCLUSION

The concept elaborated in this work proved to be successful. Oligoesters having a random sequence of substituted hydroquinones and isosorbide with propargyl endgroups were capable in individual cases of forming a stable GJ texture which allowed fixation by thermal cure at temperatures below 240°C. Particularly interesting is the formation of bright yellow colors observed for oligoesters of biphenyl-4,4′-dicarboxylic acid. When the approach of the present work is compared with the first approach based on the diesters **1a–c**, the second approach seems to be somewhat less attractive. The synthesis of the diesters **1a–c** requires the same chemicals and the same number of synthetic steps. However, the yields are considerably higher and it is easier to vary the color of the GJ textures by a variation of the amount of **2** used for the doping of **1a–c**.

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