Structure and Liquid Crystalline Properties of Poly(azomethine-ester)s

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ABSTRACT: A series of polyesters having azomethine groups in the main chain was synthesized and ability of the polymers to formation of thermotropic mesophase was investigated.

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One condition necessary for organic compounds to exhibit thermotropic liquid crystalline properties is the molecule with rod-like or disc-like structure. It is known that such structures cause an increase in the melting point of a compound. This is also the case for polymers but polymers may start to decompose before reaching the melting point. One method for lowering the high melting points of rod-like polymers is the introduction of flexible aliphatic units into their chains. This may also be achieved by using monomers with pendant groups but it should be kept in mind that the behavior of the pendant groups is made complicated by steric and polar effects.^{1,2} Steric effects generally results in reducing the thermal stability of the mesophase. On the other hand, substituted units, in which the pendant groups impart on increased polarizability and stronger dipolar interactions between the mesogenic groups, can have stronger intermolecular attractions, which would lead to higher thermal stabilities of both the crystalline and liquid crystalline phases.

In this work, both these methods were used and the influence of the structure of the rod-like monomer and the length of the aliphatic chain in the polymer on the melting point and mesomorphic temperature range are discussed. The polymers were obtained by polyconden-

sation of two series of dihydroxy-azomethine compounds with aliphatic diacids: sebacic and decanoic.

EXPERIMENTAL

Monomers

Dihydroxyazomethine compounds were synthesized in the reaction of 4-hydroxybenzaldehyde (0.2 mol) or vanillin (0.2 mol) with the proper diamine (0.1 mol) in boiling toluene (500 ml) and in the presence of *p*-toluenesulfonic acid (0.05 g).^{3,4} The crude product was crystallized from *n*-butyl alcohol. Some properties of the dihydroxyazomethine compounds whose structures were confirmed by mass spectroscopy, elemental analysis, IR and UV spectra are given in Table I.

Sebacoyl dichloride was synthesized by a reaction of sebacic acid with an excess of thionyl chloride and distilled before use. Dodecanedioyl dichloride was prepared by the reaction of diacid with oxalyl chloride.

Model Compounds

Model compounds were synthesized by the reaction of the dihydroxyazomethine compounds (0.0025 mol) with benzoyl chloride (0.005 mol) in dichloromethane (20 ml) in the presence of triethylamine (0.005 mol). The

Table I. Properties and UV maximum absorption bands, $\lambda_{\max}$ (nm) of dihydroxyazomethine compounds

No.	Ar	Yield	Melting point	UV maximum absorption bands/nm				
		%	°C	E ₁	E ₂	B	R	K
<div>HO- -CH=N-Ar-N=CH- -OH</div>								
1		50.0	264—265	205	225	287	—	357
2		75.0	313—314	206	220	290	—	350
3		67.6	285—286	208	221	281	320	359
<div><div>H₃CO- -OH</div>CH=N-Ar-N=CH-<div> -OCH₃</div></div>								
4		80.0	194—197	207	236	287	—	363
5		84.0	230—232	207	232	288	—	360
6		67.0	229—231	210	235	283	322	360

Table II. Phase transition temperatures of model compounds

No.	Ar	T_m	T_i	ΔT
		°C	°C	°C
1		215—218	330	112
2		217—220	350	130
3		277—280	330	50
4		228—230	280	50
5		231—233	320	87
6		233—235	260	25

crude product was crystallized from anisol. Phase transition temperatures of the model compounds are shown in Table II.

Polycondensation

The polycondensation reaction was carried out by the low-temperature solution method as follows. Into 0.005 mol of a dihydroxyazomethine compound and 0.010 mol of triethylamine in 25 ml of dichloromethane 0.005 mol of an acid chloride in 25 ml of dichloromethane was added at 20°C over a period of 5 min. After 3 h of stirring the reaction mixture was poured into 100 ml of ethanol and filtered. The polyesters were dried and then extracted (Soxhlet apparatus) with boiling ethanol for 8 h and dried. The properties of the polymers are presented in Tables III and IV.

Measurements

Infrared spectra were taken in nujol with a UR-20 (Zeiss apparatus).

The UV spectra were measured in methanol at a concentration of 10^{-5} mol l⁻¹ with a Specord (Zeiss apparatus).

The mass analysis was made using a LKB 9000 spectrometer, the energy of the electron beam was 70 eV and the source temperature,

Table III. Properties of sebacic acid polyesters

Ar	Yield %	$\eta_{red}^{\dagger}$ dl g ⁻¹	T_m °C	T_i °C	ΔT °C	T_d °C
$\left[\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{Ar}-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{O}-\text{C}(=\text{O})-(\text{CH}_2)_8-\text{C}(=\text{O}) \right]_n$
60	0.31	240—250 [237]	320 [320]	70	340
55	0.25	decomp.	—	—	—
70	0.22	235—240 [235]	310 [305]	70	330
$\left[\text{O}-\text{C}_6\text{H}_3(\text{OCH}_3)-\text{CH}=\text{N}-\text{Ar}-\text{N}=\text{CH}-\text{C}_6\text{H}_3(\text{H}_3\text{CO})-\text{O}-\text{C}(=\text{O})-(\text{CH}_2)_8-\text{C}(=\text{O}) \right]_n$
43	0.11	110—120	—	—	—
49	0.13	220—230	320	90	320
46	0.16	160—180	—	—	—

[†] Determined at a concn of 1 g/100 ml in concd sulfuric acid at 20°C. The temperatures detected by DSC appear in the square brackets.

290°C.

The polymers were observed for their phase transition temperatures and texture in a crystal phase using a polarizing microscope equipped with a hot stage (Boetius apparatus). For some polymers, the transition temperatures were determined by a differential scanning calorimeter (Perkin-Elmer DSC-2) at a heating rate of 10 K min⁻¹ under dry nitrogen flow.

The thermogravimetric measurements were performed in air at 1 atm on a derivatograph (F. Paulik, J. Paulik, L. Erdley) at a heating rate of 10 K min⁻¹, using a Pt-Pt/Rh thermocouple.

RESULTS AND DISCUSSION

The structures of the dihydroxyazomethine compounds were confirmed by elemental and mass analysis and the IR and UV spectroscopy methods. The infrared spectra showed the

presence of a band characteristic of $-\text{CH}=\text{N}$ bond at 1610—1640 cm⁻¹, $-\text{OH}$ group at 3500 cm⁻¹, 1380 cm⁻¹ and bands characteristic of aromatic rings at 830 cm⁻¹, 1450 cm⁻¹, 1510 cm⁻¹ and 1600 cm⁻¹. In the UV spectra of the dihydroxyazomethine compounds, there were few absorption bands (Table I). Compounds having only phenylene ring exhibited four absorption bands, E₁, E₂, B, and K, and those with naphthalene rings, and additionally R band.^{7,8} The UV absorption bands of the dihydroxyazomethine compounds were very little influenced by structure. Compounds with methoxy backbone groups shifted little bathochromically compared to the proper bands of their unsubstituted analogs. The results of elemental and spectroscopic analyses confirmed the structure of the model compounds. In the infrared spectra of the model compounds, absorption bands characteristic of $-\text{CH}=\text{N}$ group (1630 cm⁻¹) and characteristic

Table IV. Properties of dodecanedioic acid polyesters

Ar	Yield %	$\eta_{red}^{\dagger}$ dl g ⁻¹	T_m °C	T_i °C	ΔT °C	T_d °C
$\left[\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{Ar}-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{O}-\text{C}(=\text{O})-(\text{CH}_2)_{10}-\text{C}(=\text{O}) \right]_n$
77	0.10	200—210	300	90	310
50	0.18	240—250	300	50	300
53	0.10	210—220	(280), 300 [270]	(60), 80	310
$\left[\text{O}-\text{C}_6\text{H}_3(\text{OCH}_3)-\text{CH}=\text{N}-\text{Ar}-\text{N}=\text{CH}-\text{C}_6\text{H}_3(\text{OCH}_3)-\text{O}-\text{C}(=\text{O})-(\text{CH}_2)_{10}-\text{C}(=\text{O}) \right]_n$
46	0.10	120—130 [125]	(200), 300	(70), 180	300
75	partly sol.	170—180	300	120	330
55	0.12	140—160 [138, 157]	(200), 310 [192]	(40), 150	310

[†] Determined at a concn of 1 g/100 ml in concd sulfuric acid at 20°C. In parentheses appear pseudoisotropization temperatures. The temperatures detected by DSC are shown in the square brackets.

of carbonyl groups in the esters (1750 cm⁻¹) were present along with absorption bands due to aromatic rings.

While melting the model compounds on a hot plate with a polarizing microscope, transitions from the solid to anisotropic liquid phase and mesophase to isotropic liquid were observed. The phase transition temperatures are shown in Table II. Melting points of the model compounds with phenyl and biphenyl structures between the azomethine groups (No. 1, 2 and 4, 5) differed very little but there was much difference in their temperatures of transition to isotropic liquids. The linear structures of the two phenyl rings influenced the rigidity and length of the molecule as evident from the higher stability of the mesophase. Condensed aromatic rings as in the case of 1,5-diamino-naphthalene derivatives (No. 3 and 6) caused a higher melting point of the proper model compound compared to the linear biphenyl

structure but acted as destabilizing agents in the temperature range of the mesophase. The mesophase temperature range of the model compounds with pendant methoxy groups was narrower than that of the unsubstituted analogs.

The dihydroxyazomethine compounds were condensed with aliphatic diacid chlorides. The polyesters were soluble only in concd sulfuric acid, making it difficult to determine the molecular weight of the polymers. Molecular weight is one factor influencing phase transition temperatures.⁵ However the reduced viscosities of the polyesters investigated did not differ very much and the molecular weight of the polymers may not differ considerably. Table III shows the properties of the polyesters from sebacic acid. In a series of polyesters without pendant groups, strong anisotropy of the melt was observed in polymers having 1,4-phenylene and 1,5-naphthylene moieties be-

tween the azomethine groups in the dihydroxy compounds. The differences in their melting and isotropization temperatures were very little. In a series of sebacic acid polyesters with methoxy backbone groups, the strong anisotropy of the melt was observed in polyesters from di-4-hydroxy-3-methoxybenzylidene-4,4'-diaminobiphenyl. In the sebacic polyester of di-4-hydroxy-3-methoxybenzylidene-1,5-diaminonaphthalene, a monotropic transition was observed but the optical anisotropy of the melt during cooling was weak. The melts of the sebacic acid polyesters exhibited nematic texture. Table IV shows the properties of the dodecanedioic acid polyesters. The longer aliphatic chains in the macromolecules cause a lowering of the melting temperatures of the polymers compared to the sebacic polyesters. The isotropization temperatures were also a little lower. The pendant methoxy groups causing a widening of the rigid part of the macromolecule brought about a lowering of the melting points of the sebacic and dodecanedioic acid polyesters compared with the unsubstituted analogs. The melts of the dodecanedioic acid polyesters exhibited nematic structures. The dodecanedioic acid polyesters with pendant methoxy groups having 1,4-phenylene and 1,5-naphthalene rings between azomethine groups exhibit pseudoisotropic phenomena. The same was observed for the dodecanedioic acid polyester of di-4-hydroxybenzylidene-1,5-diaminonaphthalene. The pseudoisotropic phenomena were identified by the tendency of the polymer melt layer to become translucent on contact with the cover glass under microscopic observation. Near the pseudoisotropization temperatures the polymer melts contained no threads characteristic of the nematic phase and showed homogeneous color across large areas between crossed polarizers. Similar microscopic observations have been reported by Millaud *et al.*⁶ for the thermotropic nematic phase of polyazomethines. The pseudoisotropization temperatures of the polyesters investigated are

presented in Table IV in parentheses.

Taking into consideration the mesophase temperature range, it may be said that the dodecanedioic acid polyesters having one phenylene ring between the azomethine groups exhibit a wider mesophase range than those with naphthalene rings. The influence of the aliphatic chain length was not very clear but in most cases, the dodecanedioic acid polyesters had a somewhat wider temperature mesophase range than the sebacic acid analogs. Usually, the mesophase range decreased with increasing flexible chain length. The reverse results observed for these polyesters may be explained by the fact that the longer aliphatic chain being the flexible structure element of macromolecule, has a stronger influence on the melting temperature than on the isotropization temperature causing the mesophase range to be wider. For most of the polyesters investigated, a darkening at the isotropization temperatures was observed and may possibly indicate the start of decomposition. The dynamic thermal analysis results confirmed the visual observation, *i.e.*, the temperature at which the polymers lose 5% of their weight (T_d in Tables III and IV) are very close to their isotropization temperatures.

For some polyesters calorimetric analyses were made. It was found that for thermally untreated samples the phase transitions were rather vaguely indicated and in the most cases, some transitions could be detected before melting points. This is probably related to the solid-solid transitions. Annealing the polyesters at the proper temperatures made it possible to read the spectrum more easily. The annealing temperatures influenced the transitions. For example, the DSC curve of dodecanedioic acid polyesters from di-4-hydroxy-3-methoxybenzylidene-1,5-diaminonaphthalene before and after annealing at 127°C for 1 h, showed peaks at 138°C, 157°C, and 192°C, but after annealing the sample at 147°C for 14 h, the peak at 138°C disappeared. The transition temperatures at which the maxi-

mum peaks in the DSC curves for the thermally untreated polymers appeared, are presented in Tables III and IV in the square brackets. A more detailed calorimetric study in relation to X-ray diffraction investigation is in progress and the results will be published in the near future.

CONCLUSION

Properties of sebacic and dodecanedioic acid polyesters having azomethine groups bound to aromatic rings in their main chains were described. Most of the poly(azomethine-esters) obtained exhibit liquid crystalline properties and form the nematic mesophase. The relationship between the macromolecular chemical structure and phase transition temperature was established. It was confirmed

that, using a longer aliphatic chain which is a flexibilizing element in the macromolecule or using monomers with pendant methoxy groups, lowers the melting and isotropization temperatures of the polyesters.

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