

SHORT COMMUNICATIONS

Synthesis of Semi-Rigid Polyesteramides Having Piperazine Ring as a Mesogenic Unit

Satoshi HONDA, Masayoshi WATANABE, Kohei SANUI,
and Naoya OGATA

*Department of Chemistry, Sophia University, 7-1 Kioi-cho,
Chiyoda-ku, Tokyo 102, Japan*

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Thermotropic liquid crystalline polyesters are processable materials having a high degree of molecular orientation and superior mechanical strength. Therefore, there are many publications on thermotropic liquid crystalline polyesters, especially liquid crystalline aromatic polyesters.^{1,2} To lower their transition temperatures for easy processing without destroying the liquid crystalline properties, the following approaches were taken: introduction of flexible aliphatic groups into the main chain; use of asymmetrically substituted monomers and preparation of copolymers containing non-linear monomers. Processable materials of liquid crystalline polyester have superior mechanical strength due to the direction of orientation, but poor mechanical strength due to vertical direction of orientation. To overcome this problem, polyesters containing amide linkages which have strong intermolecular interaction are proposed. But there are few publications on thermotropic liquid crystalline polyesteramides, since they have high melting points with poor thermal stability.

In this study, polyesteramides containing both different number of methylene group and *trans*-2,5-dimethyl piperazine into the main chain were synthesized and the effects of flex-

ible methylene length on their thermal transition temperatures were investigated.³

A series of polyesteramides containing both different numbers of methylene groups and *trans*-2,5-dimethyl piperazine in the main chain was synthesized as follows: various diols with different numbers of methylene groups ($n=2-10$) were reacted with a double molar quantity of terephthaloyl chloride in dry chloroform containing a slight excess of triethylamine by refluxing for 1.5 h under nitrogen. After cooling to room temperature *trans*-2,5-dimethyl piperazine was added dropwise to the reaction mixture, followed by stirring at 50°C 1.5 h under nitrogen. The reaction mixture was poured into ethanol to precipitate the polymer. The polymer was filtered, washed with water and ethanol and subsequently dried under vacuum at room temperature for 72 h. The synthetic route is schematically represented in Figure 1. The polymers were identified by elemental analysis and ¹H NMR, which revealed the polymers obtained to have the expected structure of polyesteramide with *trans*-2,5-dimethyl piperazine as the mesogenic unit. The results of the polycondensation are summarized in Table I. Solution viscosities of the polymers were determined at a concentration of 0.1 g/10 cm³ in *m*-cresol at 30°C.

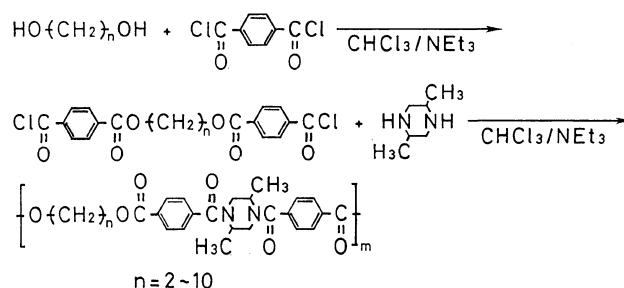


Figure 1. Synthesis of polyesteramides.

Table I. Synthesis and characterization of polyesteramides

n	Yield %	η_{inh}^a 100 cm ³ g ⁻¹	Elemental analysis/%					
			C		H		N	
			Found	Calcd	Found	Calcd	Found	Calcd
2	61.7	0.28	65.06	66.35	5.38	5.10	6.08	6.45
3	74.3	0.40	65.41	66.95	5.94	5.39	6.00	6.25
4	74.6	0.39	66.26	67.52	6.00	5.67	5.68	6.06
5	75.6	0.44	65.56	68.05	6.46	5.92	5.56	5.88
6	74.9	0.44	67.46	68.56	6.56	6.16	5.34	5.71
7	73.4	0.45	68.01	69.03	6.80	6.39	5.31	5.55
8	78.2	0.49	68.46	69.48	7.03	6.61	5.05	5.40
9	75.4	0.54	69.04	69.91	7.11	6.81	4.92	5.26
10	75.3	0.45	69.60	70.31	7.36	7.01	4.75	5.12

^a Measured at 0.1 g/10 cm³ in *m*-cresol at 30°C.

Their thermal, dynamic mechanical, and optical properties in melted state were measured by differential scanning calorimetry (DSC), Vibron Dynamic Viscoelastometer, and polarizing optical microscopy with a hot stage, respectively.

The thermal properties were investigated by DSC (Rigaku Denki 8058 and 8055 C1) at a heating rate of 20°C min⁻¹. DSC thermograms for semi-rigid polyesteramides ($n=5-10$) are shown in Figure 2. It was confirmed from the results of dynamic mechanical measurements that the lowest endothermic peak in each DSC curve corresponds to the glass transition.

The glass transition temperature (T_g) and two endothermic peaks (T_1 , T_2) were observed in thermograms for a series of polyesteramides. The polymers became sticky liquids

above T_1 , which appeared at lower endothermic peaks. The sticky liquids showed birefringent domains under a shear modulus between the temperatures of T_1 and T_2 , and became isotropic liquids above the temperature of T_2 . These results indicate the endothermic peak at T_1 to correspond to the melting transition from crystal to liquid crystal and the peak at T_2 to the clearing transition which may be the transition from the liquid crystal to the isotropic liquid. However, on cooling at 10°C min⁻¹, neither T_1 nor T_2 observed, showing the crystallization of these semi-rigid polyesteramides not to take place easily.

Plots of T_g , T_1 , T_2 against number (n) of methylene groups of a repeating unit in semi-rigid polyesteramides are shown in Figure 3,

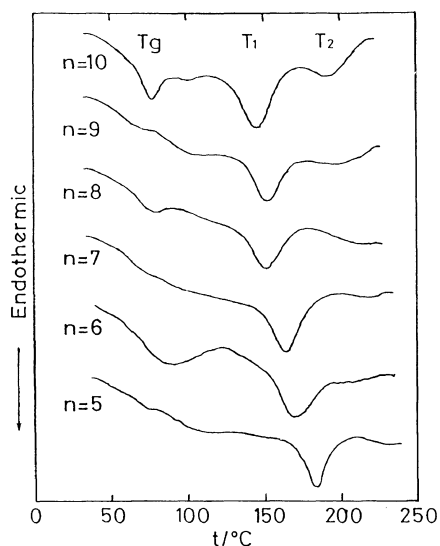


Figure 2. DSC thermograms for polyesteramides ($n = 5-10$) on heating at $20^{\circ}\text{C min}^{-1}$.

which indicates that T_g , T_1 , and T_2 of the series of polyesteramides tend to decrease on increasing the number of methylene groups between the ester groups. Their transition temperatures can be controlled by varying methylene length in the polyesteramide main chain.

Figure 4 shows the relationship between the number (n) of methylene group of polyesteramides and enthalpy or entropy changes in their transitions at T_1 . Figure 4 shows regular odd-even effects against the number (n) of methylene groups between ester groups on the enthalpy and entropy changes of transitions at T_1 . In addition, it should be noted that the clearing enthalpy and entropy changes of transition at T_2 are considerably smaller than those of the transition at T_1 for semi-rigid polyesteramides. This means that their liquid crystal phases are unstable. However, birefringence could be observed under a shear modulus at temperatures between T_1 and T_2 . The development of the birefringent domain took place with time only under an appropriate shear modulus in the case of semi-rigid polyesteramides. That is, *trans*-2,5-dimethyl piperadine used as a mesogenic group is not rigid enough

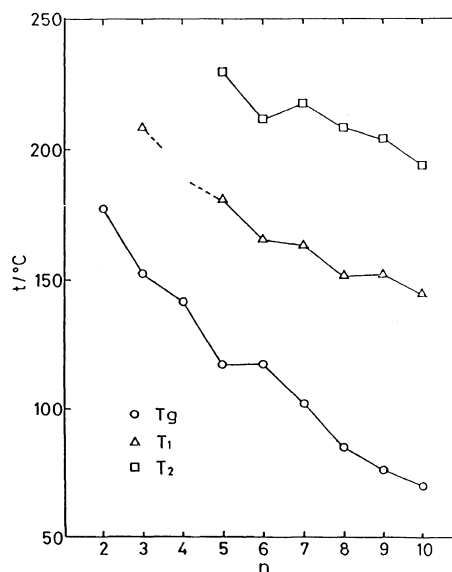


Figure 3. Plots of T_g , T_1 , T_2 against the number of methylene groups of a repeating unit in polyesteramides.

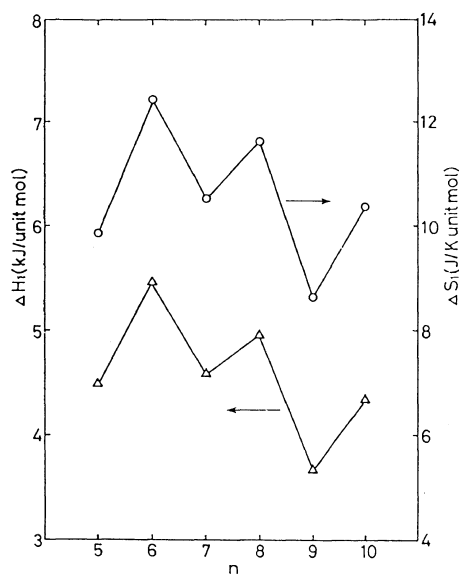


Figure 4. Relationship between the number (n) of methylene groups of a repeating unit in polyesteramides and the enthalpies or entropies of their T_1 transitions.

for the stable thermotropic liquid crystal phase. However, growth of the birefringent domain indicates the polymer chains capable

of being oriented with time under a shear modulus and this polyestaramides has liquid crystalline-like properties.

From the DSC experiments and polarizing optical microscopic observations we conclude that T_g , T_1 , and T_2 can be controlled by varying the number of methylene groups between the ester groups of polyestaramides and birefringence, since the liquid crystal phase could be observed under a shear modulus at temperatures between T_1 and T_2 .

Studies of thermotropic liquid crystal behavior for these polyestaramides and their X-ray studies are now in progress. These results will be reported in the near future.

REFERENCES

1. W. Jerome Jackson, Jr., *Br. Polym. J.*, **12**, 154 (1980).
2. J.-I. Jin, S. Antoun, C. Ober, and R. W. Lenz, *Br. Polym. J.*, **12**, 132 (1980).
3. S. Honda, M. Watanabe, K. Sanui, and N. Ogata, *Polym. Prepr. Jpn.*, **37**, 1538 (1988).