

Studies on the Synthesis and Properties of Thermotropic Liquid Crystalline Copoly(amide-ester-imide) Derived from *N*-(Hydroxyphenyl)phthalimide-4-carboxylic Acid with Amino Acid

CHIEN-HUI LI,^{1,*} AY JUNG,² AY-LING LIANG,³ and TEH-CHOU CHANG³

¹Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu 31015, Taiwan, Republic of China; ²Nanya Junior College of Technology, Chung Li, Taiwan 32034, Taiwan, Republic of China;

³Department of Chemical Engineering, Chung Yuan Christian University, Chung Li, Taiwan 32023, Republic of China

SYNOPSIS

Three series of copoly(amide-ester-imide)s were prepared from amino acid (4-aminobenzoic acid, 3-aminobenzoic acid, or 6-aminohexanoic acid) and *N*-(4-hydroxyphenyl)phthalimide-4-carboxylic acid (M1), *N*-(3-hydroxyphenyl)phthalimide-4-carboxylic acid (M2), or *N*-(2-methyl-4-hydroxyphenyl)phthalimide-4-carboxylic acid (M3) in the presence of diphenylchlorophosphate (DPCP) and pyridine as direct condensation agents. The inherent viscosities of copoly(amide-ester-imide)s were in the range of 0.13–0.95 dL/g. Thermotropic liquid crystalline (LC) behavior of these polymers was examined by differential scanning calorimetry (DSC) and optical polarizing microscopy. These copoly(amide-ester-imide)s (**IIa**, **IIc**, **IIIa**, and **IIIc**) polymerized from 3-aminobenzoic acid or 6-aminohexanoic acid with M1 or M3, respectively, showed thermotropic liquid crystalline behavior in the range of 190–426°C. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Liquid crystalline (LC) polymers have become a subject of scientific interest. Their molecular self-orientation ability opens up a wide range of applications as high-performance materials. For the processing of these polymers, some structural modifications have to be made to depress the melting transition temperatures.

The commercial thermotropic LC copolyesters (Vectra) prepared by 4-hydroxybenzoic acid (4-Hybe) with 6-hydroxy-2-naphthoic acid demonstrate that incorporation of a crankshaft structure into the poly(4-Hybe) chain reduces the melting point to such an extent that mechanical processing becomes feasible at temperatures below 400°C.^{1,2} The structure of imide monomer [*N*-(4-hydroxy-

phenyl)phthalimide-4-carboxylic acid] resembles to some extent the crankshaft structure of naphthalene.³ The copolymerization by incorporation of imide groups may exhibit a thermotropic LC property. Thus, the copoly(ester-imide)s derived from *N*-(4-carboxyphenyl)-4-acetoxypthalimide with 4-acetoxybenzoic acid have been reported by Kricheldorf et al.^{3,4} However, they suggest that the poly[*n*-(4-hydroxyphenyl)trimellitic acid] unit is not a suitable building block for LC polyester, because it raises the melting point up to temperatures where decomposition takes place.

Amide linkages are not often used to synthesize thermotropic LC polymers because the high degree of hydrogen bonding associated with these groups increases intermolecular attraction to the point that mesomorphism usually cannot occur.⁵ Therefore, it is difficult to synthesize a thermotropic LC polyamide-ester-imide. Nevertheless, there are many reports in previous studies discussing the development of thermotropic LC

* To whom correspondence should be addressed.

polymers in which the main chains contain amide groups.⁶⁻¹³

In this study, the copoly(amide-ester-imide)s are synthesized by direct polycondensation. The structures of these monomers and polymers are given in Schemes I and II. The processing problems due to a high melting point and, to a large degree, to interchain hydrogen bonding of copoly(amide-ester-imide)s, are expected to be overcome by

- incorporating substituent groups,
- incorporating *meta*-substituted benzene structures, and
- incorporating flexible aliphatic spacers.

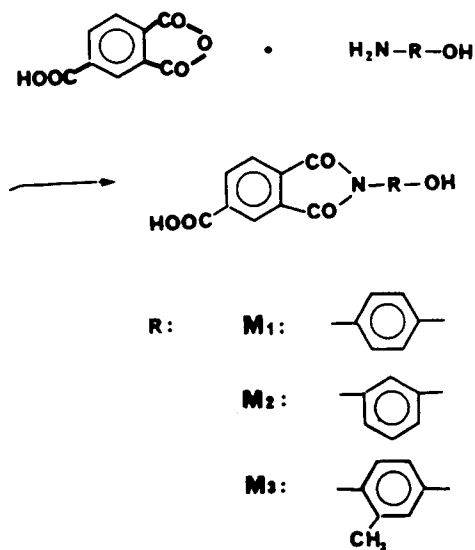
Their thermotropic LC properties were also studied.

EXPERIMENT

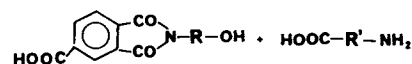
Materials and Instrumental Measurements

Commercial trimellitic anhydride (TMA) (Janssen), 3-aminophenol (Merck), 4-aminophenol (Merck), 3-methyl-4-aminophenol (Merck), 4-aminobenzoic acid (Merck), 3-aminobenzoic acid (Merck), 6-aminohexanoic acid (Merck), and diphenylchlorophosphate (Merck) were used without purification. Pyridine was purified by distillation over KOH and stored over a 4 Å molecular sieve.

IR spectra, ranging from 4000 to 400 cm^{-1} , of the solid samples of the synthesized monomers and



Scheme 1.



POLYMER	R'	R
Ia		
Ib		
Ic		
IIa		
IIb		
IIc		
IIIa	$-(\text{CH}_2)_5-$	
IIIb	$-(\text{CH}_2)_5-$	
IIIc	$-(\text{CH}_2)_5-$	

Scheme 2.

polymers were obtained by the KBr method using a Jasco-FTIR-7000 spectrophotometer. The inherent viscosities were measured with an Ubbelohde viscometer in *N,N*-dimethylacetamide (DMAC) (5 wt % LiCl) at 30°C ($C = 0.5$ g/dL). DSC measurements were conducted with a DuPont 2000 instrument in Al pans at a heating rate of 20°C/min.

Monomer Synthesis

N-(4-Hydroxyphenyl)phthalimide-4-carboxylic Acid (M1)

M1 was synthesized from 4-aminophenol and trimellitic anhydride (TMA) according to the method reported by Kurita and Matsuda.¹⁴ $M_p = 326^\circ\text{C}$ (dec).

N-(3-Hydroxyphenyl)phthalimide-4-carboxylic Acid (M2)

M2 was synthesized from 3-aminophenol and trimellitic anhydride according to the method reported by Dicke et al.¹⁵ $M_p = 302\text{--}304^\circ\text{C}$; IR (KBr): 1777,

1671, and 1388 cm^{-1} (imide $\text{C}=\text{O}$); 1717 cm^{-1} ($\text{Ar}-\text{C}=\text{O}$).

ANAL: Calcd for $\text{C}_{15}\text{H}_9\text{NO}_5$: C, 63.61%; H, 3.20%; N, 4.95%.

Found: C, 63.34%; H, 3.33%; N, 4.87%.

***N*-(2-Methyl-4-hydroxyphenyl)phthalimide-4-carboxylic acid (M3)**

Trimellitic anhydride (0.3 mol) and 3-methyl-4-aminophenol (0.3 mol) were heated in 400 mL *N,N*-dimethylformamide to 120°C for 2 h. After cooling, acetic anhydride (0.4 mol) was added and heating to 120°C was continued for 2 h. The cooled reaction mixture was then poured into ice water and the precipitated product was isolated by filtration. The crude product was purified by ethanol, yielding 28%; Mp = 302–303°C; IR (KBr): 1781, 1711, and 1388 cm^{-1} (imide $\text{C}=\text{O}$).

ANAL: Calcd $\text{C}_{16}\text{H}_{11}\text{NO}_5$: C, 64.65%; H, 3.70%; N, 4.71%.

Found: C, 63.64%; H, 3.73%; N, 4.53%.

Polymer Synthesis

A solution of diphenylchlorophosphate (DPCP) (13 mmol), pyridine (20 mL), and LiCl (10 mmol) was stirred at room temperature for 30 min and was then added dropwise for 10 min to a hot solution (preheated at 120°C for 5 min) containing amino acid 5 mmol (4-aminobenzoic acid, 3-aminobenzoic acid, or 6-aminohexanoic acid) and *N*-(hydroxyphenyl)phthalimide-4-carboxylic acid (M1, M2, or M3) 5 mmol. The final solution was heated at 120°C for 3 h under stirring and was then poured into methanol to precipitate the polymer. The precipitated polymer was filtered, refluxed in boiling methanol and water (50/50 v/v), filtered, and then dried at 110°C under vacuum.

RESULTS AND DISCUSSION

Polymer Synthesis

Three series of novel copoly(amide-ester-imide)s were prepared from amino acid (4-aminobenzoic acid, 3-aminobenzoic acid, or 6-aminohexanoic acid) and *N*-(hydroxyphenyl)phthalimide-4-carboxylic acid (M1, M2, or M3) in the presence of diphenylchlorophosphate (DPCP) and pyridine as a direct condensation agent. The inherent viscosities and thermal analyses are given in Table I. The yields of copoly(amide-ester-imide)s were in the range of 91–

96% and inherent viscosities were in the range of 0.13–0.95 dL/g. The IR spectra data for the copoly(amide-ester-imide)s are also shown in Table I. The IR spectra of all the polymers were found to be qualitatively identical. A typical IR spectrum curve for copoly(amide-ester-imide) (IIa) is shown in Figure 1. The presence of a cyclic imide group is indicated by the IR bands at 1781, 1719, and 1381 cm^{-1} , at 1719 cm^{-1} for aryl ester, and that at 723 cm^{-1} due to deformational vibration of the cyclic imide. The absorption of the ester carbonyl at 1719 cm^{-1} overlapped that of the imido carbonyl group. The presence of a $\text{C}-\text{O}-\text{C}$ band of the ester group is indicated by the peak appearing at 1210 cm^{-1} . Bands of amide groups appear at 3350 and 1665 cm^{-1} . The results confirmed the expected structure of copoly(amide-ester-imide).

Thermotropic Liquid Crystalline (LC) Properties of copoly(amide-ester-imide)s

The phase behavior of copoly(amide-ester-imide)s are summarized in Table I according to DSC data and polarizing microscopic observation. The copoly(amide-ester-imide)s, IIa, IIc, IIIa, and IIIc, exhibited stirred opalescence and melt birefringence under a polarizing microscope equipped with a heating stage. Therefore, it was concluded that thermotropic liquid crystalline copoly(amide-ester-imide)s were indeed synthesized in this study. The melting points of copoly(amide-ester-imide)s measured by DSC were confirmed by the polarizing microscope. Copoly(amide-ester-imide) Ia derived from 4-aminobenzoic acid with *N*-(4-hydroxyphenyl)phthalimide-4-carboxylic acid (M1) is insoluble in all common solvents. No melting is detectable by microscopic observation up to temperatures in the range 400–480°C, where thermal degradation takes place. The copoly(ester-imide)s derived from *N*-(4-carboxyphenyl)-4-acetoxyphthalimide with 4-acetoxybenzoic acid did not exhibit thermotropic LC properties.^{3,4} Therefore, the results of copoly(amide-ester-imide) Ia confirmed the observation by Kricheldorf et al.^{3,4}

To reduce the melting temperature, the first method was to proceed with incorporating substituent groups. Polymer Ic derived from 4-aminobenzoic acid with *N*-(2-methyl-4-hydroxyphenyl)phthalimide-4-carboxylic acid (M3) was infusible under microscopic observation. DSC measurement did not show any obvious transition peak. Copolymerization and incorporation of kinks was the second method used to lower the melting point.

Table I The Properties of Copoly(amide-imide-ester)s

Polymer	η_{inh} (dL/g)	LC Phase (°C)	Transition Temperature	IR Character			
				Amide	Imide	Ester	—CH ₂ —
Ia	0.42	<i>e</i>	—				
Ib	0.19	<i>e</i>	—				
Ic	0.95	<i>e</i>	—				
IIa	^d	290–426	280	3350 1665	1781, 1719 1381, 723	1719 1210	
IIb	0.13	None	210	3342 1671	1779, 1723 1379, 725	1723 1209	
IIc	0.17	260–350	253	3326 1671	1781, 1725 1381, 727	1725 1234	
IIIa	0.16	190–310	191	3312 1649	1775, 1717 1383, 725	1717 1218	2936 2864
IIIb	0.25	None	176	3370 1650	1775, 1725 1377, 723	1725 1218	2936 2860
IIIc	0.24	200–300	203				

^a Inherent viscosity measured with 0.5 g/dL in DMAC (5% LiCl) at 30°C.

^b As observed under a polarized microscope with a heating stage.

^c From DSC, first heating, 20°C/min heating rate.

^d Insoluble.

^e Infusible.

Polymer **Ib** was prepared from *N*-(3-hydroxyphenyl)phthalimide-4-carboxylic acid (M2) with 4-aminobenzoic acid. As shown in Table I, polymers **Ib** and **Ic** had a similar result. They revealed that the rigid structure of the imide group and the hydrogen-bonding effect induced by amide groups on the polymer chain would raise the melting temperature of the polymers.

The third method was to proceed by changing the position of the kink group. The copoly(amide-ester-imide)s **IIa** and **IIc**, derived from 3-aminobenzoic acid with M1 and M3, respectively, showed nematic thermotropic LC behavior under optical polarizing microscopic observation. When the polyester main chains contained more than 35 mol % of the 1,3-phenylene unit, the linearities of the polymer chains were drastically decreased and no LC phases were observed.¹⁶ However, in this study, polymers **IIa** and **IIc** containing 50 mol % kink structure (1,3-phenylene unit) exhibited thermotropic LC behavior. This suggested that the crank-shaft imide groups compensated for the nonlinearity of the central kink groups to permit a greater colinearity. Polymers **IIa** and **IIc** showed anisotropic melt at 280 and 253°C, respectively. This method was successful in reducing

their melting temperature and retaining their LC property.

From DSC measurements, polymers **IIb** and **IIIb** derived from M2 showed one sharp endotherm at 210 and 176°C, respectively. No LC phase was found from polarizing microscopic observation. It revealed that polymers **IIb** and **IIIb** did not exhibit thermotropic LC properties due to the presence of nonlinear units causing the axial ratio to be reduced and chain packing to be frustrated and the mesophase stability to be decreased.¹⁷

The fourth method was to proceed with incorporation of flexible aliphatic groups. To examine the effect of flexible aliphatic groups on LC properties, copoly(amide-ester-imide)s were prepared by 6-aminohexanoic acid with M1–M3. As shown in Table I, the LC phases of polymers **IIIa** and **IIIc** were in the range of 190–310°C as measured by the polarizing microscope. The T_m of the copoly(amide-ester-imide)s **III** derived from 6-aminohexanoic acid were decreased as compared with those of the copoly(amide-ester-imide)s derived from 3- or 4-aminobenzoic acid. This revealed that the flexible aliphatic units on polymers **IIIa** and **IIIc** decreased the T_m and retained the LC property successfully.

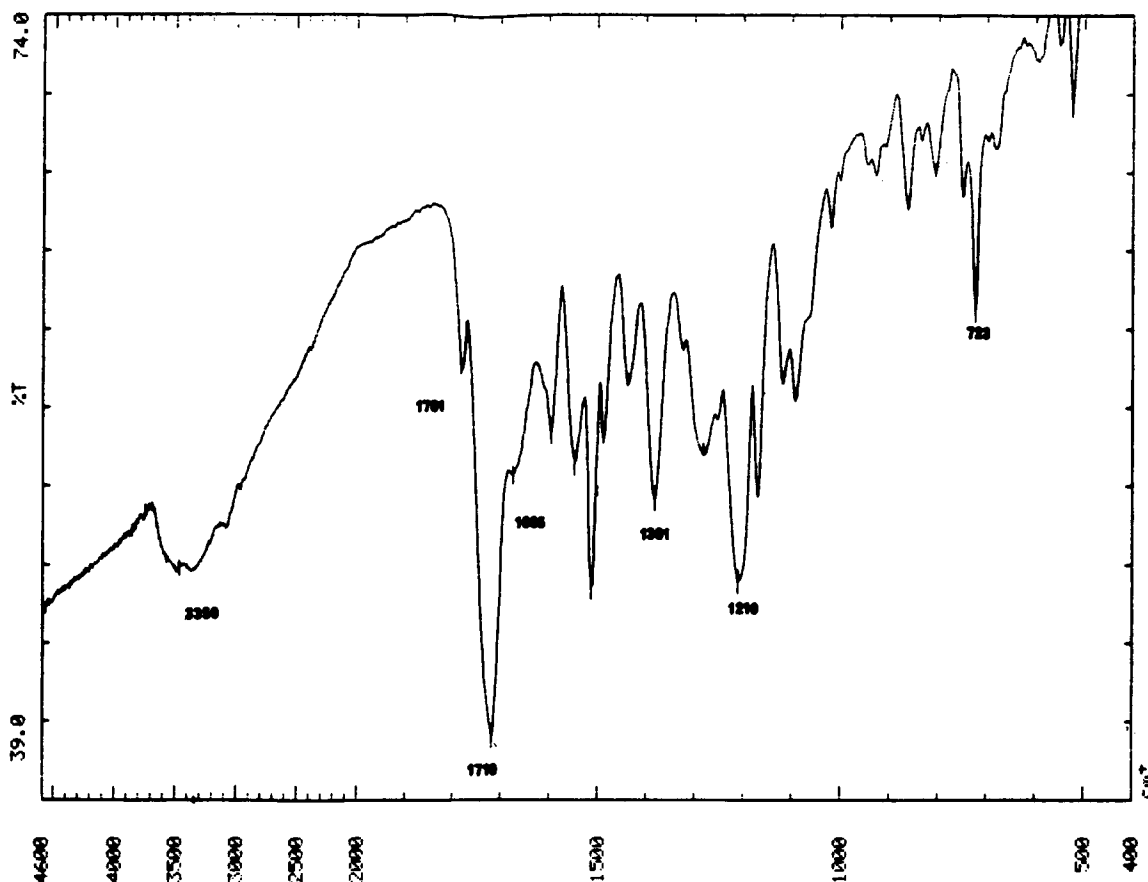


Figure 1 The IR spectrum of copoly(amide-ester-imide) IIa.

These copoly(amide-ester-imide)s (IIa, IIc, IIIa, and IIIc) derived from 3-aminobenzoic acid or 6-aminohexanoic acid with M1 or M3, respectively, showed thermotropic LC behavior. However, copolymers IIb and IIIb derived from M2 did not exhibit an LC property. The results of this study demonstrate that the mesophase stabilities are in the order of M1, M3 > M2.

CONCLUSION

1. Thermotropic liquid crystalline copoly-(amide-ester-imide)s could be prepared by 3-aminobenzoic acid or 6-aminohexanoic acid with M1 or M3 in the presence of DPCP and pyridine used as direct condensation agent.
2. Methods of copolymerization and incorporation of kinks or flexible aliphatic groups were successful in reducing their melting temperature and retaining their liquid crystalline property.

3. The mesophase stabilities are in the order of M1, M3 > M2.

The authors are indebted to the National Science Council and the Ministry of Economic Affairs of the Republic of China for financial support of this work (NSC 82-115-C-253-501-E).

REFERENCES

1. E. W. Choe and G. W. Galundann, Ger. Pat. 3,015,386 (1981); *Chem. Abstr.*, **94**, 8558f (1981).
2. M. Y. Cao and B. Wunderlich, *Polym. Sci. Polym. Phys. Ed.*, **25**, 521 (1985).
3. H. R. Kricheldorf, G. Schwarz, and W. Nowatzky, *Polymer*, **30**, 936 (1989).
4. H. R. Kricheldorf and R. Pakull, *J. Polym. Sci. Polym. Lett. Ed.*, **23**, 413 (1985).
5. (a) J. R. Evans, R. A. Orwoll, and S. S. Tang, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 971 (1985). (b) M. A. Osman, *Polymer*, **28**, 713 (1987). (c) M. A. Osman, *Macromolecules*, **19**, 1874 (1986).

6. C. H. Li and T. C. Chang, *J. Polym. Sci. Polym. Chem. Ed.*, **28**, 3625 (1990).
7. C. H. Li and T. C. Chang, *J. Polym. Sci. Polym. Chem. Ed.*, **29**, 361 (1991).
8. A. L. Liang, K. Y. Hsu, and T. C. Chang, *Eur. Polym. J.*, **28**, 783 (1992).
9. A. L. Liang, K. Y. Hsu, C. H. Li, and T. C. Chang, *Polymer*, **33**, 2217 (1992).
10. C. H. Li, K. Y. Hsu, and T. C. Chang, *J. Polym. Sci. Polym. Chem. Ed.*, **29**, 1447 (1991).
11. C. H. Li, K. Y. Hsu, and T. C. Chang, *J. Polym. Sci. Polym. Chem. Ed.*, **31**, 1119 (1993).
12. C. H. Li, H. P. Cheng, T. C. Chang, and T. Y. Chu, *J. Polym. Sci. Polym. Chem. Ed.*, **31**, 1125 (1993).
13. T. C. Chang and C. H. Li, *J. Polym. Sci. Polym. Chem. Ed.*, **31**, 1423 (1993).
14. K. Kurita and S. Matsuda, *Makromol. Chem.*, **184**, 1223 (1983).
15. H. R. Dicke, J. Genz, V. Eckhardt, and L. Botenbruch, U.S. Pat. 4,954,605 (1990).
16. H. R. Kricheldorf and D. Lubbers, *Macromolecules*, **21**, 551 (1988).
17. R. W. Lenz and J. I. Jin, *Macromolecules*, **14**, 1405 (1981).

Received September 23, 1994

Accepted November 3, 1994