

Liquid Crystalline Thermosets 1. Synthesis and Characterization of Liquid Crystalline Thermosets' Precursor Polymers

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ABSTRACT: The synthesis of three novel liquid crystalline monomers and their corresponding linear polymers is described. The chemical structures of the monomers **M-1**~**M-3** were confirmed by Fourier transform infrared (FT-IR) and proton nuclear magnetic resonance (¹H NMR) spectroscopy. Their liquid crystalline properties and phase behavior were studied by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and thermogravimetric analyses (TGA). Monomers **M-1**~**M-3** and polymers **P-1**~**P-3** all exhibited nematic texture. Moreover, **M-3** and **P-3** also showed smectic A phase besides nematic phase. Experimental results demonstrated that the melting temperatures, glass transition temperatures, and clearing temperatures of **M-1**~**M-3** and **P-1**~**P-3** decreased with the spacer length from $n=0$ to $n=6$. TGA showed that the temperatures at which 5% weight loss occurred were greater than 275°C for **P-1**~**P-3**.

KEY WORDS Liquid Crystalline Thermosets / Nematic Phase / Smectic Phase /

Over the last several years, liquid crystalline thermosets (LCTs) have attracted considerable interest due to their electrical, mechanical, and optical properties for advanced applications in numerous areas, such as matrix for composites, surface coatings, microelectronics packing, high-temperature adhesives, and nonlinear optics.^{1–11} LCTs generally consist of central mesogenic core end-capped with functional groups capable of reacting to provide a crosslinked network. Similar to conventional thermosets, LCTs are infusible and insoluble solid, which has high glass transition temperature and high modulus at room temperature. LCTs have shown potential for improved thermal stability, orientational stability, low coefficient of thermal expansion, low shrinkage on curing, low dielectric loss, enhanced dielectric strength, and enhanced reaction rates due to the close proximity of the reactive groups. Moreover, potential processing advantages also exist with these new materials. LCTs are classified according to the polymerization method employed: (i) polyaddition reaction of mesogenic epoxy resin with hardening compounds; (ii) thermal polymerization of a variety of functional groups; and (iii) photopolymerization. At present, numerous attempts have been made to study LCTs. Recently, many kinds of LCTs have been prepared by polymerizing monomers and oligomers with vinyl,¹² acrylate,^{13, 14} methacrylate,^{15, 16} ethynyl,^{3, 9, 17, 18} epoxy,^{19–21} nadimide,²² and maleimide²³ functional groups to explore their application.

It is well known that acrylate monomers easy form

polymers by free radical polymerization, whereas allyl monomers polymerize hardly. Thus the use of acrylate–allyl monomers, where both acrylate and allyl groups are combined in the same molecule, can firstly obtain soluble precursor polymers by free radical polymerization, then these linear precursor polymers can form LCTs by special polymerization at liquid crystalline state.

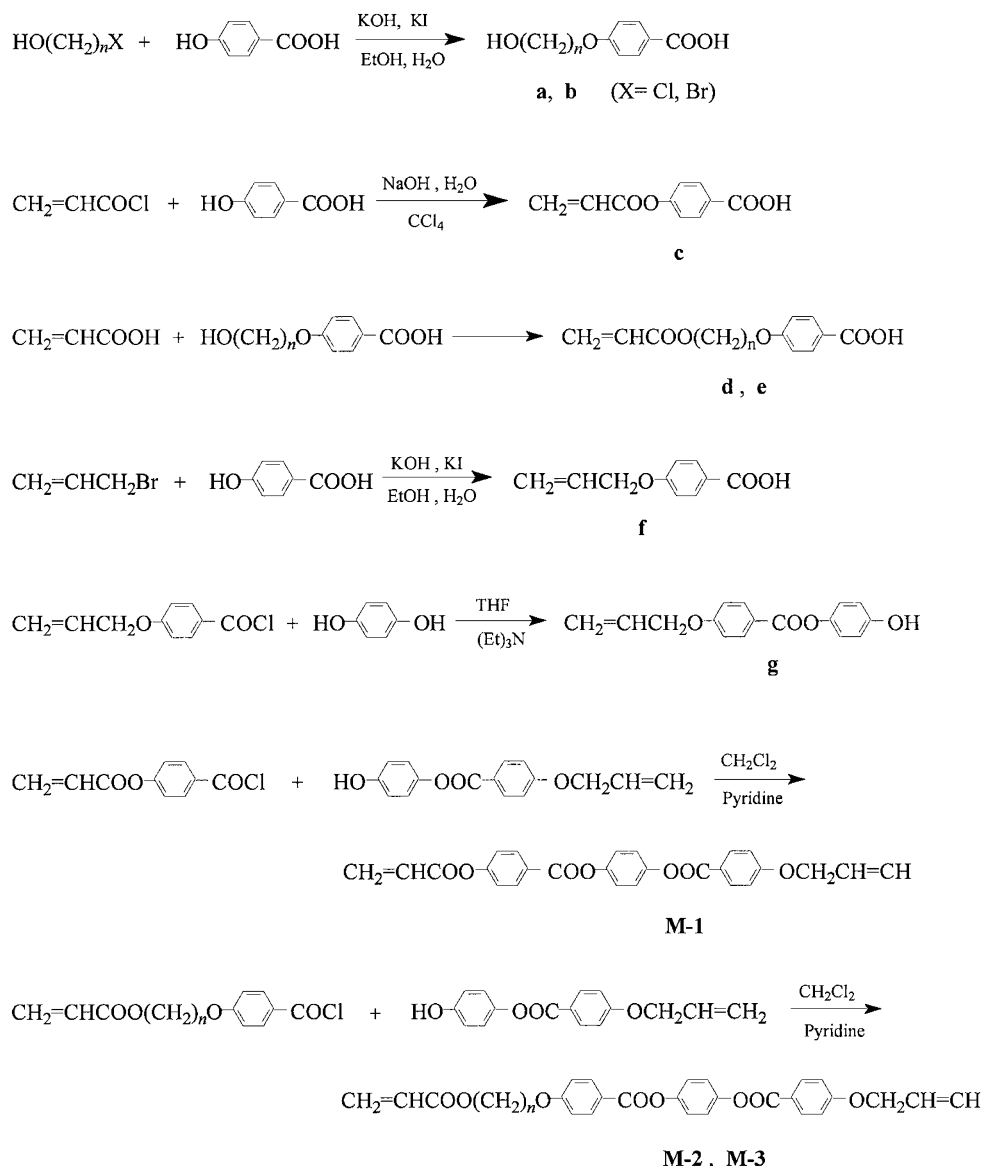
Our goal was the synthesis and characterization of novel LCTs with acrylate–allyl functional groups. In this study, we firstly synthesized and characterized novel liquid crystalline monomers with acrylate–allyl difunctional groups and their corresponding LCTs' precursor polymers. Their optical textures and phase behavior were investigated with POM, DSC, and TGA. The effect of the flexible spacer length on the phase transition temperatures and phase type was discussed.

EXPERIMENTAL

Materials

Chloro-ethanol was purchased from Shenyang Xinxi Chemical Reagent Co. (China). 4-Hydroxybenzoic acid was purchased from Beijing Fuxing Chemical Industry Co. (China). 1,6-Hexanediol was purchased from Beijing Hongyu Chemical Industry Co. (China). Toluene used in the hydrosilylation reaction was first refluxed over sodium and then distilled. All other solvents and reagents were purified by standard methods.

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Scheme 1. Synthetic routes of monomers.

Characterization

Fourier transform infrared (FT-IR) spectra were measured on a Nicolet 510 FT-IR spectrometer (Nicolet Instruments, Madison, WI, USA). ^1H NMR spectra (300 MHz) were recorded on a Varian WH-90PFT spectrometer (Varian Associates, Palo Alto, CA, USA). Phase transition temperatures and thermodynamic parameters were determined using a PerkinElmer DSC-7 (PerkinElmer, Foster City, CA, USA) equipped with a liquid nitrogen cooling system. Heating and cooling rates were $20^\circ\text{C min}^{-1}$. Phase transition temperatures were taken during the second heating and first cooling scans. Thermal stability of the polymers under atmosphere was measured with a PerkinElmer TGA-7 thermogravimetric analyzer at $20^\circ\text{C min}^{-1}$ heating rate. A Leitz Microphot-FX (Leitz, Wetzlar, Germany) polarizing optical microscope equipped with a Mettler FP 82 hot stage and FP 80 central processor were used to

observe phase transition temperatures and analyze mesomorphic properties for liquid crystalline monomers and polymers through observation of optical texture.

Synthesis of Monomers

The synthetic routes of liquid crystalline monomers **M-1**~**M-3** are shown in Scheme 1. 4-(Acryloyloxy-*n*-alkyloxy)benzoic acid and 4-hydroxyphenyl-4'-allyloxybenzoate were prepared according to literature procedures reported by Hu.^{24,25} Yields and phase transition temperatures of the intermediate compounds are summarized in Table I. The structural characterization of **M-1**~**M-3** are listed in Table II.

4-Acryloyloxybenzoyl-4'-allyloxybenzoyl-*p*-benzenediol bisate (**M-1**), 4-(2-acryloyloxyethyloxy)benzoyl-4'-allyloxybenzoyl-*p*-benzenediol bisate (**M-2**), 4-(6-acryloyloxyhexyloxy)benzoyl-4'-allyloxybenzoyl-*p*-benzenediol bisate (**M-3**). The monomers **M-1**~**M-3**

were prepared by the same method. The synthesis of **M-1** is described below.

4-Acryloyloxybenzoic acid (9.6 g, 0.05 mol) was reacted at 40 °C with thionyl chloride (15 mL) containing a few drops of *N,N*-dimethylformamide and trace of *p*-hydroxyanisole for 4 h. Excess thionyl chloride was removed under reduced pressure to give the acid chloride. The acid chloride was dissolved in dry methylene chloride (10 mL), and added dropwise to a cold solution of 4-hydroxyphenyl-4'-allyloxybenzoate (13.5 g, 0.05 mol) in pyridine (4 mL) and methylene chloride (30 mL). After reacting for 8 h, the precipitate was removed by filtration, and the crude product was precipitated by adding ethanol to the filtrate.

Synthesis of Polymers

For the synthesis of polymers **P-1**~**P-3**, the same method was adopted. The synthesis of **P-2** is given as an example.

The polymer **P-2** was synthesized by radical polymerization of 4-(2-acryloyloxyethoxy)benzoyl-4'-allyloxybenzoyl-*p*-benzenediol bisate in dry toluene using α,α' -azobisisobutyronitrile (AIBN, 2 mol% to the

monomer) as an initiator at 60 °C for 24 h under nitrogen conditions. The polymer was obtained by precipitation with methanol, washed with hot ethanol, and dried under vacuum.

RESULTS AND DISCUSSION

Synthesis

The structural characterization of the monomers **M-1**~**M-3** was in agreement well with the prediction. 4-(Acryloyloxy-*n*-alkyloxy)benzoic acid (**c**, **d**, and **e**) and 4-hydroxyphenyl-4'-allyloxybenzoate (**g**) were prepared according to a route described by Hu.^{24,25} The synthetic methods of **M-1**~**M-3** were same. Firstly, activation of **c**, **d**, and **e** was obtained with thionyl chloride, then reacted with **g** in present of pyridine in methylene chloride to prepare target monomers with acrylate-allyl difunctional groups. FT-IR spectra of **M-1**~**M-3** showed characteristic ester C=O stretching bands at 1736–1730 cm⁻¹, olefinic C=C absorption bands at 1647–1640 cm⁻¹, and aromatic at around 1610 and 1509 cm⁻¹. ¹H NMR spectra of **M-1**~**M-3** showed multiplet at 8.27–6.95 ppm and 6.35–5.30 ppm attributed to aromatic and olefinic protons, respectively. In addition, **M-3** exhibited a multiplet at 1.87–1.51 ppm, corresponding to methylene and methyl protons.

It is well known that allyl monomers polymerize hardly by free radical polymerization because of the dominant effect of chain transfer reaction.²⁶ However, acrylate monomers easy form polymers by free radical polymerization, where allyl groups are incorporated in the polymer backbone. Thus the use of acrylate-allyl monomers, where both acrylate and allyl groups

Table I. Yields and phase transition temperatures of intermediate compounds

Compounds	<i>n</i>	Transition temperature/°C	Yields/%
a	2	K 180 I	64
b	6	K 132 I	58
c	–	K 175 I	72
d	2	K 141 I	90
e	6	K 90 N 98 I	87
f	–	K 165 I	69
g	–	K 139 I	88

K, solid; N, nematic; I, isotropic.

Table II. Yields and Characterization of Monomers

Monomer	<i>n</i>	Yield (%)	IR (KBr) cm ⁻¹	¹ H NMR chemical shifts (CDCl ₃ , δ , ppm)
M-1	0	62	3073 (=CH); 2965, 2837 (CH ₃ , CH ₂); 1730 (C=O); 1647 (C=C); 1607, 1509 (Ar)	4.67 (t, 2 H, –OCH ₂ –); 5.33–5.49 (m, 4 H, CH ₂ =CHCH ₂ –, CH ₂ =CHCOO–); 6.07 (m, 1 H, CH ₂ =CHCH ₂ –); 6.35 (m, 1 H, CH ₂ =CHCOO–); 7.02–8.27 (m, 12 H, Ar–H)
M-2	2	53	3070 (=CH); 2969, 2845 (CH ₃ –, –CH ₂ –); 1735 (C=O); 1640 (C=C); 1608, 1512 (Ar–)	3.79 (t, 2 H, –CH ₂ CH ₂ O–); 4.27 (t, 2 H, –COOCH ₂ –); 4.63 (t, 2 H, =CHCH ₂ O–); 5.30–5.48 (m, 4 H, CH ₂ =CHCH ₂ –, CH ₂ =CHCOO–); 6.05 (m, 1 H, CH ₂ =CHCH ₂ –); 6.26 (m, 1 H, CH ₂ =CHCOO–); 6.95–8.18 (m, 12 H, Ar–H)
M-3	6	47	3076 (=CH); 2938, 2863 (CH ₃ –, –CH ₂ –); 1736 (C=O); 1643 (C=C); 1610, 1513 (Ar–)	1.51–1.87 [m, 8 H, –(CH ₂) ₄]; 3.75 (t, 2 H, –CH ₂ CH ₂ O–); 4.18 (t, 2 H, –COOCH ₂ –); 4.62 (t, 2 H, =CHCH ₂ O–); 5.31–5.48 (m, 4 H, CH ₂ =CHCH ₂ –, CH ₂ =CHCOO–); 6.01 (m, 1 H, CH ₂ =CHCH ₂ –); 6.20 (m, 1 H, CH ₂ =CHCOO–); 6.96–8.17 (m, 12 H, Ar–H)

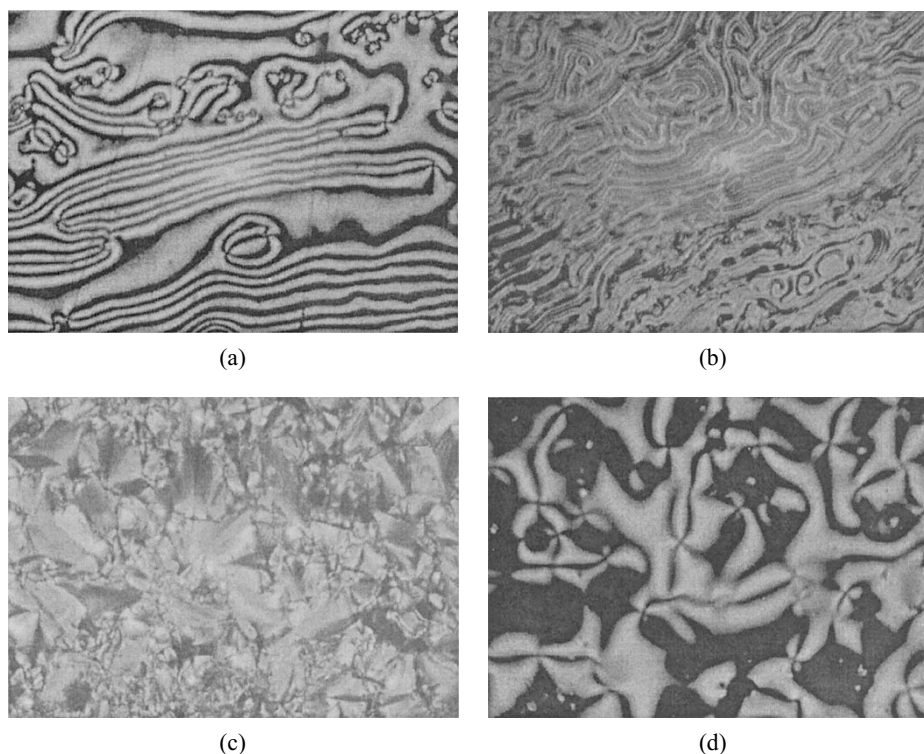


Figure 1. POM micrographs of monomers (200 \times): (a) Schlieren texture of **M-1** at 220 $^{\circ}$ C; (b) Threaded texture of **M-2** at 134 $^{\circ}$ C; (c) Fan-shaped texture of **M-3** at 83 $^{\circ}$ C; (d) Schlieren texture of **M-3** at 189 $^{\circ}$ C.

are combined in the same molecule, can obtain soluble polymers. Then, these linear precursor polymers undergo special polymerization in liquid crystalline phase, which can result in polymer networks.

Texture Analysis

In general, liquid crystalline materials show nematic phase or smectic phase, which mainly depends on relative strength of molecular transverse attractive force and terminal attractive force. When molecular transverse attractive force is predominant, liquid crystalline materials show smectic phase. Conversely, liquid crystalline materials show nematic phase. However, when the strength of these two kinds of force is about equal, both smectic and nematic phase can appear.²⁷

Polarizing optical microscopy (POM) observation results showed that the monomers **M-1**~**M-3** and polymers **P-1**~**P-3** exhibited enantiotropic nematic phase during heating and cooling cycles. In addition, **M-3** and **P-3** also exhibited smectic A phase besides nematic phase, the reason for which is that the strength of molecular terminal attractive force decreases with spacer length from $n=0$ to $n=6$. When monomers **M-1** and **M-2** were heated to the melting temperatures (T_m), the typical nematic threaded texture and schlieren texture appeared. The mesomorphic properties disappeared at the clearing temperatures (T_i). **M-3** was heated to T_m , the smectic fan-shaped texture occurred. As heating continued, the fan-shaped tex-

ture transformed gradually to nematic schlieren texture. Photomicrographs of **M-1**~**M-3** are shown in Figures 1a, 1b, 1c, and 1d. Similar to **M-1**~**M-3**, polymers **P-1** and **P-2** exhibited the nematic threaded texture and schlieren texture, **P-3** exhibited the smectic fan-shaped texture and nematic schlieren texture during the heating and cooling cycles. Photomicrographs of **P-1** are shown in Figures 2a and 2b as an example.

Thermal Analysis

The thermal properties of monomers **M-1**~**M-3** and polymers **P-1**~**P-3** were determined by differential scanning calorimetry (DSC) measurement. Both the second heating and the first cooling cycles were recorded. The phase transition temperatures and corresponding enthalpy changes of **M-1**~**M-3** and **P-1**~**P-3** are summarized in Tables III and IV, respectively.

DSC heating thermograms of **M-1** and **M-2** showed the melting transition and a nematic to isotropic phase transition, and thermograms of **M-3** displayed, in turn, the melting transition, a smectic to nematic phase transition, and a nematic to isotropic phase transition, which agrees with POM observation results. As can be seen from the data listed in Table III, the phase transition temperatures and phase type of the monomers were influenced by the spacer length. For **M-1**~**M-3**, T_m decreased from 141.2 to 76.5 $^{\circ}$ C, and T_i decreased from 230.0 to 199.0 $^{\circ}$ C with the spacer length from $n=0$ to $n=6$. However, the mesomorphic temperature ranges

(ΔT) increased from 88.8 to 122.5 °C because T_i decreased less than T_m . On the heating scans of **P-1**~**P-3**, a glass transition and a nematic to isotropic phase transition were observed. In addition, a smectic to nematic phase transition between the glass transition temperature (T_g) and T_i was also observed on DSC curve of **P-3**. Above all phase transitions were reversible during

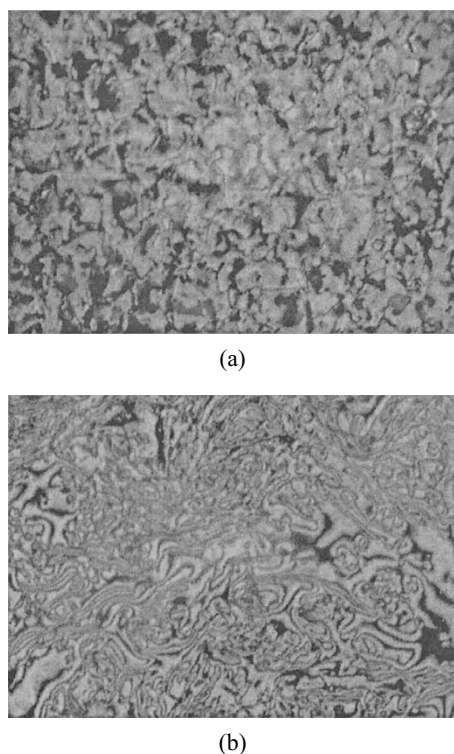


Figure 2. POM micrographs of **P-1** (200 \times): (a) Threaded texture at 127 °C; (b) Schlieren texture at 253 °C.

the heating and cooling cycles. The phase transition temperatures determined by DSC were consistent with those observed by POM.

In general, the mesogenic units are usually attached to the polymer backbone *via* a flexible spacer, which is generally an aliphatic hydrocarbon chain containing more than two methylene units. The polymer backbone and mesogenic units have antagonistic tendencies: the polymer backbone is driven towards a random coil-type configuration, whereas the mesogenic units stabilize with long-range orientation order. The flexible spacer decouples the mesogenic side groups from the polymer backbone. According to the data listed in Table IV, the flexible spacer length had a considerable influence on the phase behavior of **P-1**~**P-3**. An increase of the spacer length made T_g decrease from 107.4 to 65.9 °C, and T_i decrease from 267.6 to 213.6 °C. In addition, ΔT of **P-1**~**P-3** were greater than those of the corresponding monomers **M-1**~**M-3**, which indicates that polymerization can result in the stabilization of mesophase.

Figure 3 shows the thermogravimetric analyses (TGA) thermograms of the polymers. The thermal decomposition temperatures (T_d) of **P-1**~**P-3** were greater than 275 °C, this indicates that LCT' precursor polymers have higher thermal stability.

CONCLUSIONS

In this study, novel liquid crystalline monomers and the corresponding linear polymers were prepared and

Table III. Phase transition temperatures of monomers

Monomers	n	Transition temperature ^a in °C (Corresponding enthalpy changes in J g ⁻¹)		Yields (%)	ΔT_1^b	ΔT_2^c
		Heating	Cooling			
M-1	0	K141.2(29.5)N230.0(0.8)I I221.8(0.5)N117.4(22.7)K		62	88.8	104.4
M-2	2	K84.2(13.2)N200.9(1.5)I I194.2(0.9)N51.8(16.8)K		53	116.7	142.4
M-3	6	K76.5(22.2)S86.5(3.7)N199.0(2.7)I I194.7(1.5)S77.1(2.2)N36.3(17.2)		47	122.5	158.4

K, solid; N, nematic; S, smectic; I, isotropic. ^aPeak temperatures were taken as the phase transition temperature. ^bMesophase temperature ranges during the heating cycle. ^cMesophase temperature ranges during the cooling cycle.

Table IV. Thermal properties for polymers

Polymer	n	Yields/%	$T_g/^\circ\text{C}$	$T_{s-n}^a/^\circ\text{C}$	$T_i/^\circ\text{C}$	ΔT^b	$T_d^c/^\circ\text{C}$
P-1	0	86	107.4	–	267.6	160.2	278.1
P-2	2	82	72.1	–	237.3	165.2	283.6
P-3	6	83	65.9	139.2	213.6	147.7	294.9

^aSmectic to nematic phase transition temperature. ^bMesomorphic temperature ranges. ^cTemperature at which 5% weight loss occurred.

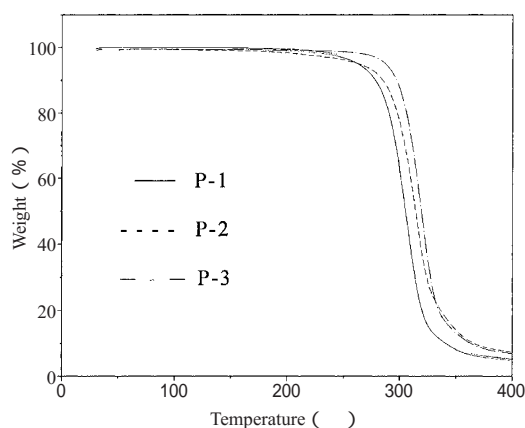


Figure 3. TGA thermograms of P-1~P-3.

characterized. All of the obtained polymers showed wider mesophase temperature ranges and higher thermal stability. Monomers **M-1~M-3** and polymers **P-1~P-3** exhibited nematic threaded texture and schlieren texture. Moreover, **M-3** and **P-3** also showed smectic fan-shaped texture besides nematic texture. The melting temperatures, glass transition temperatures and clearing temperatures of monomers and polymers decreased with increasing the spacer length.

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