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Synthesis and Thermal Properties of Poly(2-Chloroethyl Glycidyl Ether)-Based Side-Chain Liquid-Crystalline Polymers

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A novel series of poly(2-chloroethyl glycidyl ether)-based side-chain liquid-crystalline copolymers has been synthesized in which the mesogenic units are biphenyl 4-methoxybiphenyl, 4-methoxyazobenzene, and N-benzylidene-4-methoxyaniline, respectively (corresponding polymers are referred to as PCBH, PCMB, PCMA, and PCBM). The structures of the compounds obtained are characterized by infrared (IR) and ¹H nuclear magnetic resonance (NMR). The thermal properties were investigated using polarized optical microscopy, differential scanning calorimetry, and X-ray diffraction analysis. The results indicate that PCMA, PCMB, and PCBM exhibit thermotropic liquid-crystalline behavior and present nematic phases with Schlieren textures. However, PCBH does not display a mesogenic phase. The decomposition temperatures of copolymers begin at 290°C.

Keywords Azobenzene; biphenyl; liquid-crystalline polymer; N-benzylidene-4-methoxyaniline; poly(2-chloroethyl glycidyl ether); thermal properties

Introduction

Side-chain liquid-crystalline polymers (SCLCPs) have great potential in a wide range of applications such as information storage [1], holographic imaging [2–4], nonlinear optics [5], collecting and extracting of some metal ions [6], which gives us a better understanding of the self-assembly in molecular systems [7,8].

SCLCPs consist of three structural units: a polymer backbone, a spacer, and a mesogenic group. The most frequently used mesogens are biphenyl, azobenzene, Schiff's base, ester and cyano, nitro, alkyl, or alkoxy groups attached as terminal units because these groups induce dipole–dipole intermolecular interactions, which contribute to the overall stability of the mesophase. The spacer connecting the mesogenic unit to the polymer backbone is regarded as an important constituent, in order to decouple the motion of the backbone component from the arrangement of the mesogenic side chains [9]. The length and flexibility of the spacer play a significant role in determining the thermal stability, phase transition temperatures,

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and corresponding enthalpy change of the copolymers, especially the order arrangement of the mesogenic groups to self-assemble from those of the main chain to adopt a random coil configuration [10].

Polyether is a flexible linear backbone. Polyepichlorohydrin is usually used as the main chain of polyether-based SCLCPs and it can react with many compounds containing a mesogenic unit to form liquid-crystalline compounds [11–15]. However, the disadvantage of polyepichlorohydrin is the absence of an extra spacer. Poly(2-chloroethyl glycidyl ether) (PCGE) can overcome it for its extra ethoxy unit in side chain, but few examples have been reported to employ PCGE as the main chain of SCLCP.

In this work, an attempt is made to synthesize PCGE-based SCLCPs by means of a nucleophilic substitution reaction of PCGE with sodium phenoxide of a mesogenic group such as biphenyl, 4-methoxyazobenzene, 4-methoxybiphenyl, and N-benzylidene-4-methoxyaniline. The study mainly focuses on the synthesis and thermal behavior of the copolymers and the effect of different mesogenic groups on thermal properties.

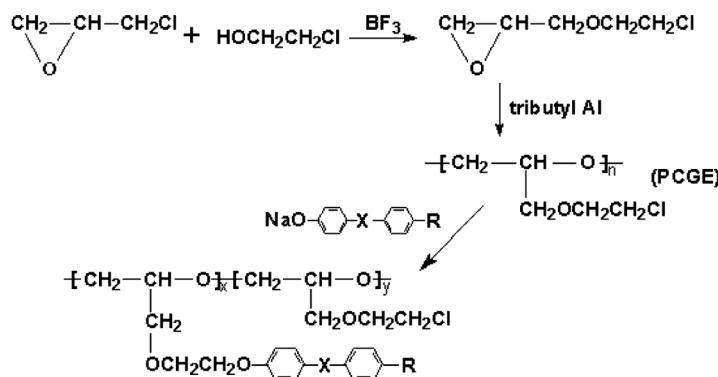
Experimental

Materials

The solution of tributyl aluminum in toluene was provided by Wuhan Organic Synthesis Limit Co., China. 4-Hydroxylbiphenyl was purchased from Alfa Aesar. All other chemicals (Shanghai Chemical Regent Co., China) used in this study were analytical grade. Ethanol was dried over magnesium and distilled. Toluene and 1,4-dioxane were refluxed with sodium and distilled. Other reagents were used without further purification.

Instruments

Infrared (IR) spectra were recorded using a Nicolet-60SXB Fourier transform infrared (FTIR) spectrometer (Nicolet, USA). ¹H nuclear magnetic resonance (NMR) (300 MHz) spectra were recorded on a Varian Mercury VX-300 (Varian, USA) in CDCl₃ solutions, using trimethyl siloxane (TMS) as internal standard. The number-average molecular weight (*M_n*) of PCGE was determined by gel permeation chromatography (GPC) using a system equipped with a Waters 2690D separation module and a Waters 2410 refractive index detector (Alliance HPLC, USA). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.3 mL min⁻¹ [13]. Waters Millennium Module software was used to calculate the molecular weight on the basis of a universal calibration curve generated by a polystyrene standard with a narrow molecular weight distribution [13]. Thermal characterization was done via differential scanning calorimetry (DSC) on a TA DSC-Q10 instrument (TA, USA). The optical textures of the mesophases were studied with an Olympus BH-2 polarizing optical microscope (POM, magnification: $\times 100$) fitted with a Linkam THMSE 600 heating stage (Olympus, Japan). The X-ray diffraction patterns were obtained using a D/MAX-III A diffractometer (Rigaku, Tokyo, Japan) with nickel-filtered Cu K α radiation, at a scanning rate of 8° min⁻¹. Thermogravimetric analysis (TGA) was conducted using a STA 449C (NETZSCH, Germany) instrument with a nitrogen atmosphere.



PCBH : R = H , X = 0 ; **PCMA**: R = OCH₃, X = N=N;

PCMB: R = OCH₃, X = 0 ; **PCBM**: R = OCH₃, X = C=N;

Scheme 1. Reaction scheme of PCGE-based copolymers.

Synthesis

The synthetic route for the preparation of polymers is outlined in Scheme 1.

4-Hydroxyl-4'-methoxybiphenyl (HMB) was prepared according to the literature [16]. Yield: 40.8%; mp: 178–180°C. ¹H NMR (CDCl₃, δ in ppm): 7.48, 6.94 (m, aromatic, 8H); 3.89 (s, OCH₃, 3H).

4-Hydroxyl-4'-methoxyazobenzene (HMA) was synthesized according to the literature [13]. Yield: 82%; mp: 140–141°C. ¹H NMR (CDCl₃, δ in ppm): 7.92, 6.94 (m, aromatic, 8H); 3.91 (s, OCH₃, 3H).

N-(4-Hydroxylbenzylidene)-4-methoxyaniline (HBM) was prepared according to the reported method [17]. Yield: 86%; mp: 172–174°C. ¹H NMR (CDCl₃, δ in ppm): 8.38 (s, -CH=N-, 1H), 7.79, 7.20, 6.91 (m, aromatic, 8H); 3.83 (s, OCH₃, 3H), shown in Fig. 1a.

2-Chloroethyl glycidyl ether was prepared using the procedures described in the literature [18]. Yield: 47.6%, bp: 60–61°C/2 mmHg, *n*_D²⁵ = 1.4492 (reported *n*_D²⁵ = 1.4492).

Polymerization of 2-chloroethyl Glycidyl Ether. 2-Chloroethyl glycidyl ether (PCGE; 20 g) was mixed with dry toluene (20 mL) and tributyl aluminum in toluene (2 mL) was added. After being stirred at 100°C under a nitrogen stream for 5 h, the mixture was poured into methanol to precipitate polymer. The resulting polymer was purified by precipitation from CHCl₃ solution into methanol and dried at 60°C in vacuum for 48 h. Yield: 65%. ¹H NMR (CDCl₃, δ in ppm): 3.73–3.53 (m), as shown in Fig. 1b. M_n = 2,347, M_w/M_n = 2.13.

Substitution of PCGE. According to a similar method described previously [19], The monomer unit (10 mmol) and sodium ethoxide (10 mmol) were mixed in dry ethanol (10 mL) and refluxed for 1 h under a nitrogen stream and then the solvent was removed. PCGE (9 mmol) dissolved in dry 1,4-dioxane (20 mL) and tetrabutylamine bromoate (1 mmol) were added. The reaction mixture was stirred at 100°C under a dried nitrogen stream for 54 h and centrifuged to remove sodium chloride, and the filtrate was poured into methanol. The crude polymer was purified by precipitation

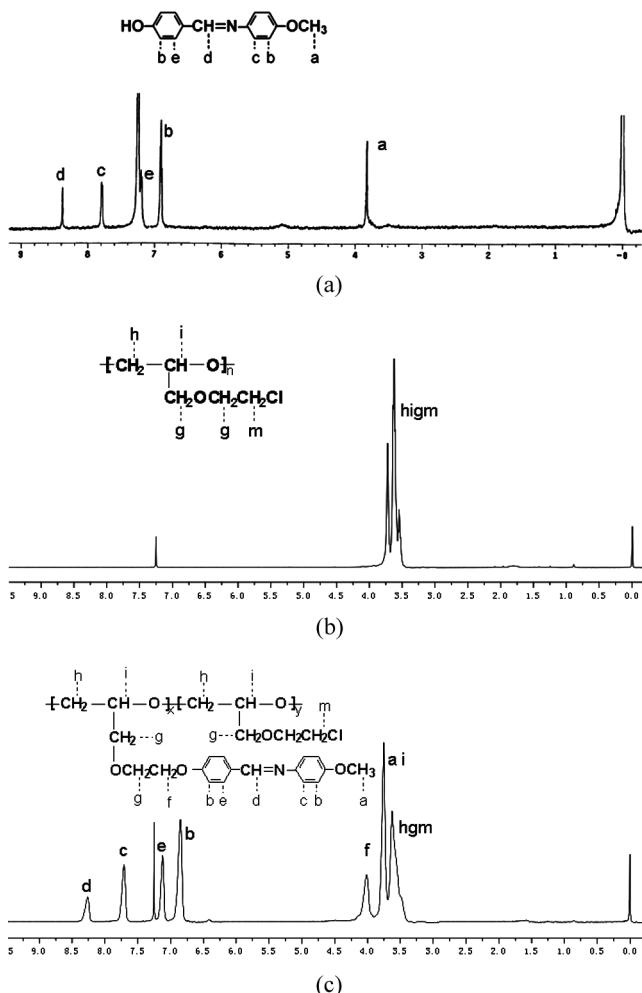


Figure 1. ¹H NMR spectra of HBM (a), PCGE (b), and PCBM (c) (CDCl₃, TMS).

from CH₃Cl into methanol. The removal of the monomer was monitored using thin-layer chromatography. Finally, the obtained copolymer was dried in a vacuum at 50°C for 48 h. Their structures were confirmed by IR and ¹H NMR.

PCBH Yield: 46%; Substitution degree: 87%. IR (KBr, cm⁻¹): 3,034 (C-H aromatic), 1608 (C=C aromatic). ¹H NMR (CDCl₃) δ(ppm): 7.49–6.92 (s, aromatic, 9H), 4.01 (s, PhOCH₂, 2H), 3.75–3.62 (s, PCGE backbone, 8.3H).

PCMB Yield: 50%; Substitution degree: 89%. IR (KBr, cm⁻¹): 3,048 (C-H aromatic), 1,610 (C=C aromatic). ¹H NMR (CDCl₃) δ(ppm): 7.38 (s, aromatic, 4H), 6.93 (s, aromatic, 4H), 4.12 (s, PhOCH₂, 2H), 3.84–3.62 (t, PhOCH₃, PCGE backbone, 11.1H).

PCMA Yield: 51%; Substitution degree: 91%. IR (KBr, cm⁻¹): 3,070 (C-H aromatic), 1,598 (C=C aromatic), 1,499 (-N=N-). ¹H NMR (CDCl₃) δ(ppm): 7.84 (s, aromatic, 4H), 6.95 (s, aromatic, 4H), 4.01 (s, PhOCH₂, 2H), 3.83–3.72 (t, PhOCH₃, PCGE backbone, 10.9H).

PCBM Yield: 50%; Substitution degree: 90%. IR (KBr, cm^{-1}): 3,065 (C-H aromatic), 1,610 (C=C aromatic), 1,496 (-C=N-). ^1H NMR (CDCl_3) δ (ppm): 8.26 (s, -CH=N-, 1H), 7.71 (s, aromatic, 2H), 7.12 (s, aromatic, 2H), 6.84 (s, aromatic, 4H), 4.02 (s, PhOCH_2 , 2H), 3.75–3.62 (t, PhOCH_3 , PCGE backbone, 11.0H).

Result and Discussion

Synthesis

The substitution degree of the mesogenic group depends on the reaction time. For PCBM, an 8% increase of substitution degree was obtained as the reaction time increased by 6 h. The substitution degree increased slightly when the reaction time was over 50 h. Therefore, the reaction time was 54 h for PCBM. The same reaction time was taken for other copolymers. The substitution degrees of mesogenic groups of the above-mentioned polymers are close to each other and do not depend on the mesogenic groups. In addition, more attention should be paid to water in the synthesis, because sodium ethoxide and sodium phenoxide react with water easily in solvent and in air and therefore affect the substitution degree and yield.

IR and ^1H NMR Characterization

The chemical structures of the synthesized monomers and copolymers were characterized by IR spectroscopy and ^1H NMR to confirm the expected reaction routes and the resulting products.

Figure 2 shows the IR spectra of HBA, PCGE, and PCMA as representative examples. From the spectra, the characteristic absorption bands at 1,499, 1,598, and $3,070\text{ cm}^{-1}$, which are attributed to -N=N-, C=C (aromatic) and C-H (aromatic), respectively, are observed in the IR spectrum of PCMA. The -OH stretching and bending vibrations at $3,050\text{ cm}^{-1}$ appears in the spectrum of HBA and disappears in the spectrum of PCMA. This demonstrates that the HBA has been successfully grafted on to the main chain of PCGE.

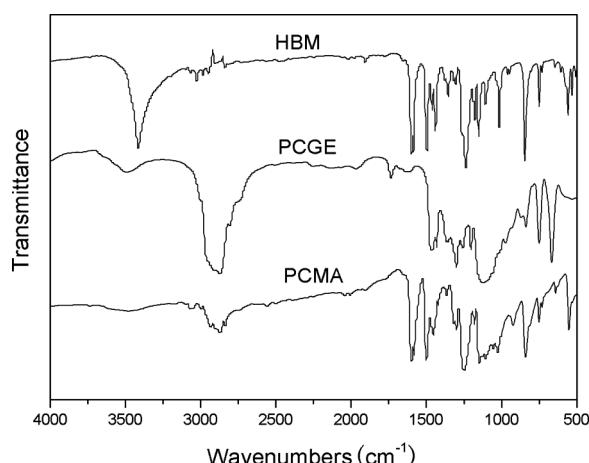


Figure 2. IR spectra of HMA, PCGE, and PCMA.

Figure 1 displays the ^1H NMR spectra of monomer HBM, polymer (PCGE), and copolymer (PCBM). The structure of monomer HBM can be identified clearly by corresponding resonance peaks, the chemical shift of the hydrogen in Schiff's base, especially, is about 8.4 ppm. Comparing the three ^1H NMR spectra, the resonance peak of $\text{H}(-\text{CH}_2\text{OAr})$ shifts from 3.8 ppm ($-\text{CH}_2\text{Cl}$ shown in Fig. 1) to 4.2 ppm due to the change of chemical environment for the hydrogen; the other protons do not change apparently in chemical shifts (δ). In addition, the shape of peaks in HBM exhibits a sharp multiplet as in Fig. 1a and become a fewer or a broad singlet in Fig. 1c, which implies that the compound characterized in Fig. 1c is a copolymer. The spectroscopic data demonstrate that the structures of all compounds are consistent with those expected. The ^1H NMR analysis confirms the attachment of the mesogenic groups onto the PEGE backbone, which is in agreement with the reaction shown in Scheme 1. The ^1H NMR spectra of PCBH, PCMB, and PCBM are similar to the model.

Thermal Properties

Thermal properties of the copolymers were examined by DSC measurement, which was carried out with heating and cooling rates at $20^\circ\text{C min}^{-1}$ under a dry nitrogen purge.

Figure 3a shows DSC trace of PCMA. The DSC traces in the second heating scan for PCBH, PCMB, and PCBM are shown in Fig. 3b. The thermal data of the copolymers are listed in Table 1 and were extracted from the second heating and cooling cycles.

PCMA exhibits two endothermic peaks at about 118.5°C ($\Delta\text{H} = 28.1\text{ J/g}$) and 133.1°C ($\Delta\text{H} = 1.9\text{ J/g}$) in the second heating scan. During the second cooling scan, on isotropic to a liquid-crystalline phase transition at about 128.4°C ($\Delta\text{H} = 1.6\text{ J/g}$) and the crystallization transition at about 87.3°C ($\Delta\text{H} = 28.1\text{ J/g}$) were observed. In Fig. 3b, PCMB and PCBM show two endothermic peaks, namely, a melting transition and a clearing transition, in the second heating scan. The results indicate that PCMA, PCMB, and PCBM possess liquid-crystalline behavior. PCBH does not

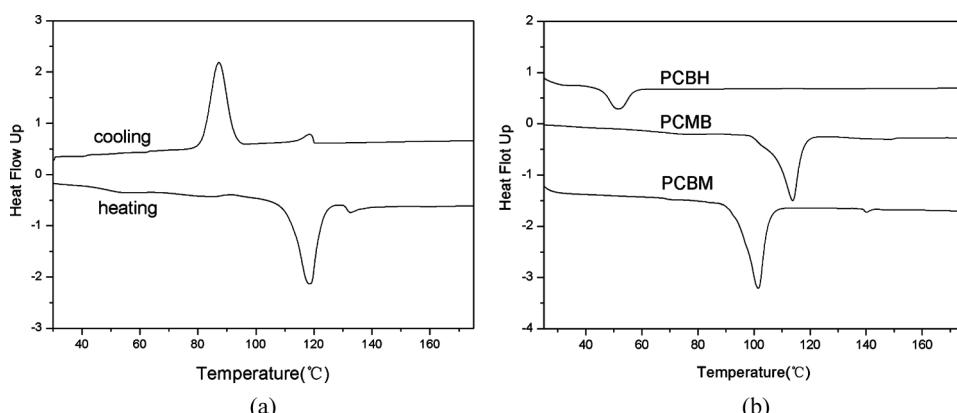


Figure 3. DSC thermogram of PCMA (a) and PCMB, PCMB, and PCBM (b) at a heating rate $20^\circ\text{C min}^{-1}$.

Table 1. Thermal transition temperature and enthalpy change of PCGE-based polymers

Sample	Substitution degree (%) ^a	Phase transition temperature (°C) and enthalpy change			
		T _m ^b (ΔH)	T _i ^c (ΔH)	T _{n-k} ^d	T _{i-n} ^e (ΔH)
PCBH	87	51.5 (8.70)	—	—	—
PCMB	89	113.8 (27.2)	148.8 (0.8)	101.5 (18.7)	128.4 (0.9)
PCMA	91	118.5 (28.1)	133.2 (1.1)	87.3 (28.0)	122.0 (1.3)
PCBM	90	101.5 (22.9)	142.1 (0.52)	98 ^f	142 ^f

^aDetermined from ¹H NMR measurements.^bMelting temperature.^cIsotropization temperature.^dTransition from nematic to crystalline.^eTransition from isotropic to nematic.^fDetermined by optical microscopy.

exhibit a thermotropic liquid-crystalline phase due to its unique endothermic peak for melting transition and without a clearing transition.

Table 1 summarizes the thermal properties of the synthesized copolymers. In the cooling scan, the phase transitions from the melting state to the solid state of PCBH and PCBM have not appeared because, as observed in our experiment, the process is very slow at ambient temperature and is unable to solidify in minutes even at rate of 5°C min⁻¹ until -20°C. On the other hand, the enthalpy changes from nematic to isotropic phase transition are too small to be found in the curves. This behavior is similar to that of compounds that have been synthesized previously [20]. Their solidifying points, therefore, can only be determined by optical microscopy.

The phase transition temperatures and corresponding enthalpy changes for these copolymers during cooling are lower and smaller than those obtained during heating, which should be due to the motion of the flexible main backbone hindering sample crystallization. The change of melting point and corresponding enthalpy change do not display apparent rule with different mesogens, which the usual behavior seen with liquid crystals will be further investigated in future.

Liquid Crystalline Textures

Polarizing optical microscopy (POM) can reveal directly the presence and type of mesophase in terms of the texture and the temperature of phase transition. In observation, the samples are heated to approximately 10°C above their clearing points and then cooled at 0.2°C min⁻¹.

POM of copolymers PCMB, PCMA, and PCBM exhibits a typical Schlieren texture, which is assigned as a nematic phase as shown in Fig. 4. The textures are obtained by cooling the isotropic phase to 131°C for PCMB, to 132°C for PCBM, and to 100°C for PCMA, respectively. PCBH is not mesogenic. Obviously, the texture is affected greatly by the mesogenic unit. The result shows that the temperature of the texture developing is approximately consistent with the second transition measured by DSC.

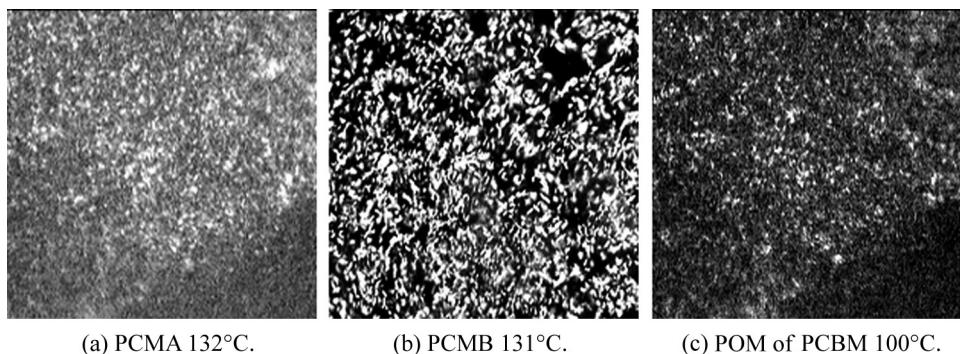


Figure 4. POM of copolymer in cooling from isotropic phase ($\times 100$). .

X-Ray Diffraction

X-ray diffraction measurement can further confirm the existence of a liquid-crystalline phase and identify the types of mesophase. The diffractograms of PCMB and PCBM are similar to that of PCMA, shown in Fig. 5 as a representative example.

Figure 5a displays the diffraction pattern obtained with powder sample at ambient temperature without special treatment and exhibits some sharp peak reflections in the wide-angle region (about $2\theta \approx 22^\circ$), indicating the complex structure similar to a quasi-crystal phase. The diffraction pattern (Fig. 5b), which was obtained by heating the sample to the liquid-crystalline phase and then quenching in a liquid nitrogen bath, presents a diffuse, broad halo in the wide-angle region and no peak was observed in the low-angle region, which implies that the polymer has no lamellar order in the direction of the molecular long axes and resembles an amorphous polymer. The result indicates the presence of a nematic mesophase.

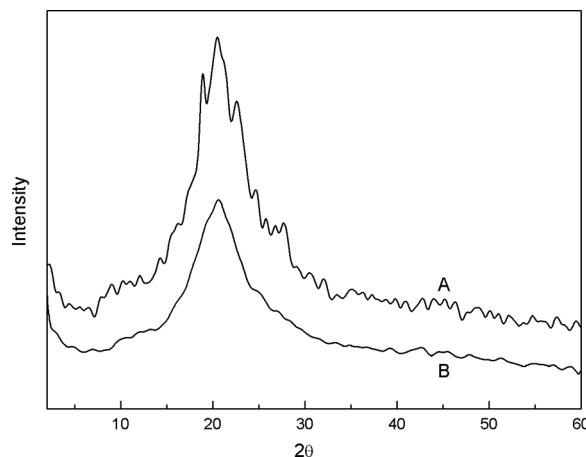


Figure 5. Wide-angle X-ray diffractograms of PCMA: (a) before quenching and (b) after quenching.

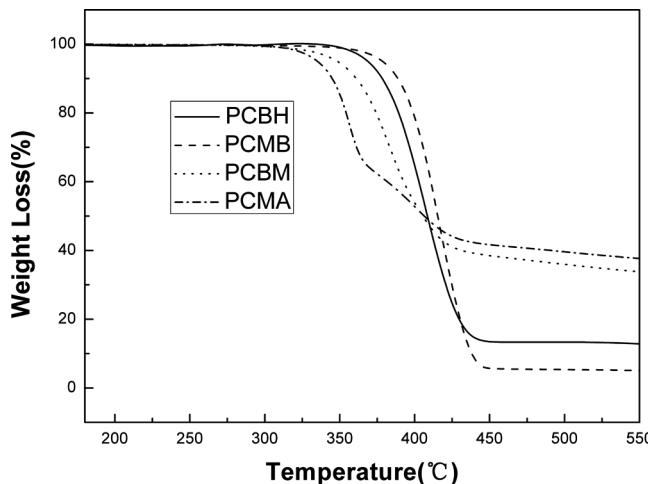


Figure 6. TGA curves of copolymers under nitrogen.

Thermal Stability

The thermal degradation properties of the PCGE-based copolymers was investigated by TGA and the measurement was carried out under a nitrogen atmosphere in the range of 50°C~600°C. The obtained TG curves are shown in Fig. 6, which exhibits the comparative thermal degradation of resulting polymers. The decomposition of PCMA and PCBM begins at near 295°C corresponding to the degradation of the azo-benzene and the Schiff's base groups. At around 350°C, the cleavage of the PCGE backbone (-OCH₂CH₂Cl) occurs. The decomposition stage, at around 420°C~440°C, may be due to cleavage of the benzene ring and the chain (-OCH₂CH₂). Obviously, the thermal stability of the copolymers is related to the structure of mesogenic groups.

Conclusion

A series of poly(2-chloroethyl glycidyl ether)-based side-chain liquid-crystalline copolymers has been synthesized by the nucleophilic substitution reaction of poly(2-chloroethyl glycidyl ether) with compounds containing a mesogenic group according to a previously developed synthetic approach. The structures of the synthesized compounds were confirmed by IR and ¹H NMR spectroscopy, which give satisfactory data corresponding to the molecular structures expected. DSC measurement, POM investigation, and X-ray diffraction studies indicate that the obtained copolymers, except for that bearing a biphenyl group, possess liquid-crystalline properties and display a nematic phase. All the results demonstrate that poly(2-chloroethyl glycidyl ether) has an ability to act as the main-chain backbone of a side-chain liquid-crystalline copolymer; nevertheless, its molecular weight is expected to be further raised in the future.

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