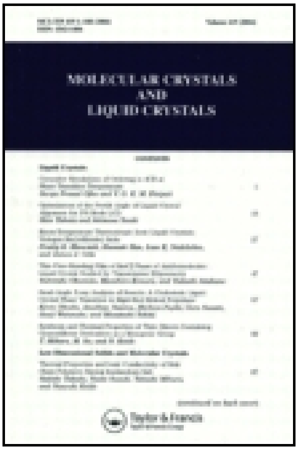

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Synthesis and Thermal Properties of Side-Chain Type Liquid Crystalline Polymers Containing Carbazolyl Group

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SYNTHESIS AND THERMAL PROPERTIES OF SIDE-CHAIN TYPE LIQUID CRYSTALLINE POLYMERS CONTAINING CARBAZOLYL GROUP

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New side-chain type liquid crystalline (LC) polymers containing carbazolyl group were synthesized. These polymers contain carbazolyl derivatives, 2-(9-methyl-carbazolyl) benzoate as a part of mesogen, and polymethacrylate, polyester, polymethylsiloxane, polymaleimides as a polymer backbone. The mesomorphic behavior and phase transition temperatures of these polymers were characterized by polarizing optical microscopy and differential scanning calorimetry (DSC) measurements. The LC phases were revealed by X-ray diffraction measurements. Polymethacrylate containing non-substituted carbazolyl moiety exhibited a smectic A_1 phase. Polymethacrylates containing nitro-substituted carbazolyl moiety exhibited a smectic A_d phase. The latter one has the high phase transition temperatures and the wide mesomorphic temperature ranges. Polyester derivatives did not show typical LC phases. Polysiloxane derivatives exhibited a smectic A_1 phase. The siloxane ring would contribute the stability of the LC phase. Polymaleimide derivative with longer methylene unit in the side chain exhibited a smectic C phase, while polymaleimide derivative with shorter methylene unit in the side chain showed a nematic phase.

Keywords: carbazole; carbazolyl derivatives; nitro-substituted carbazole; side-chain type liquid crystalline polymers

INTRODUCTION

Since the photoconductive property of poly(N-vinylcarbazole) (PVCz) was discovered, carbazole and carbazolyl derivatives have attracted a much attention [1]. The PVCz and other carbazolyl derivatives exhibit some other properties such as luminescent property [2–4], hole-transporting property

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[2–4], etc [5,6]. Therefore, some applications depending on the multifunction of carbazolyl derivatives are expected in recent years. For example, research for organic electroluminescent (EL) materials [3,4] with hole-transporting property and luminescent property is carried out. Moreover, application as organic photorefractive (PR) materials [5–7] with photoconductivity and non-linear optical property has also been developed.

Enhancement of photoconductivity, hole-transporting property, and photorefractive property are expected by the arrangement of molecules. For example, there are some reports that carrier mobility of liquid crystalline compounds containing photoconductive moiety is 100–1000 times higher than the conventional materials [8,9]. The improvement of the carrier mobility plays an important role for EL materials. Furthermore, for PR materials, organic PR polymer exhibited the high diffraction efficiency compared to the inorganic materials because of the orientational enhancement effect [7]. This effect is based on the reorientation of the molecules. Therefore, there are some examples for PR effects using liquid crystal compounds [10,11].

We synthesized new side-chain type liquid crystalline polymers containing carbazolyl moiety as the part of mesogen to obtain the functional polymer as shown in Table I. We also investigated the thermal properties of these polymers.

RESULT AND DISCUSSION

Polymethacrylate Derivatives (PM11Cz, PM′11Cz, PM11CzNO$_2$)

Thermal properties of polymethacrylate derivatives are shown in Table II. The molecular weight of PM11Cz is 25,000. It has glass transition temperature (Tg) and smectic-isotropic phase transition temperature (T_{SmI}) at 56°C and 174°C on heating process, respectively. The entropy change from the isotropic phase to the smectic phase (ΔS_{SmI}) is $2.0 \times 10^{-2} JK^{-1}g^{-1}$. A focal-conic fan texture as shown in Figure 1a was observed in the temperature range between Tg and T_{SmI} of PM11Cz, and its texture was frozen below Tg on cooling process. The X-ray diffraction pattern of the polymer displayed the strong diffraction peak in the small angle region at 2.5° corresponding to the layer spacing of 35.3 Å and unassigned weak diffraction peak in the small angle region at 5.1°. The calculated value of the length of the side chain is about 32 Å. Therefore, mesomorphic phase structure of the polymer would be assigned to the smectic A_1 phase. The carrier mobility and alignment behavior of this polymer have been already studied [12].

PM′11Cz has Tg at 102°C on heating process. It decomposed at the temperature around 205°C. Probably, the high rigidity of the mesogen

TABLE I Chemical Structures of Synthesized Polymers

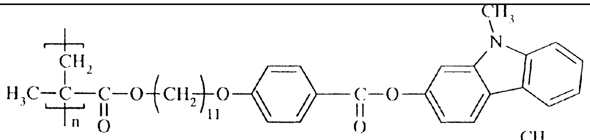
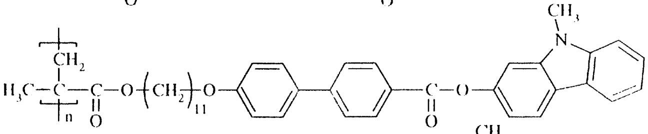
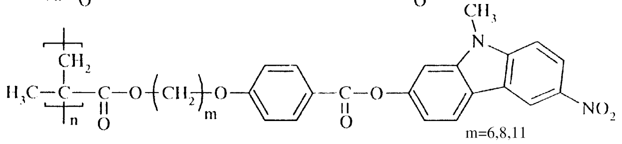
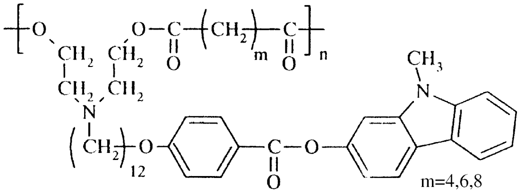
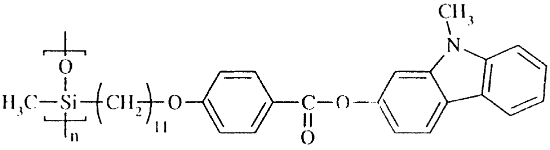
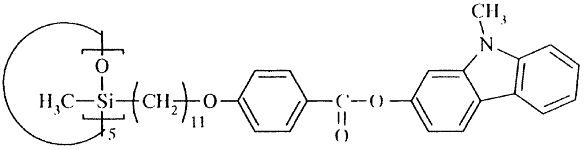
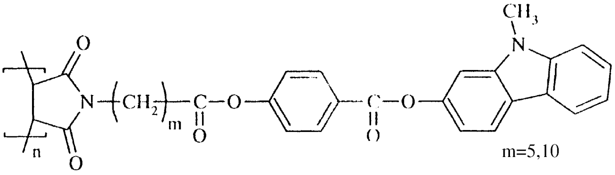
Polymer	Chemical structures
PM11Cz	
PM′11Cz	
PMmCzNo$_2$	 m=6,8,11
PmN12Cz	 m=4,6,8
PsiO11Cz	
PSiC11Cz	
PMImCz	 m=5,10

TABLE II Molecular Weights and Thermal Properties of Polymethacrylate Derivatives

Polymer	Molecular weight (Mn)	Phase transition temperature (°C)	$\Delta S_{SmI}(JK^{-1}g^{-1})^{1)}$
PM11Cz	25,000	$g \underset{54}{\overset{56}{\rightleftarrows}} Sm \underset{165}{\overset{174}{\rightleftarrows}} I$	2.0×10^{-2}
PM′11Cz	---2)	$g \xrightarrow{102} Sm \xrightarrow{205}$ Decomp.	---
$PM11CzNO_2$	---2)	$g \underset{78}{\overset{79}{\rightleftarrows}} Sm \underset{210}{\overset{214}{\rightleftarrows}} I$	7.7×10^{-3}

g: glassy, Sm: smectic phase, I: isotropic phase, Decomp.: thermal decomposition.
1) Smectic - isotropic phase transition entropy change.
2) Insoluble in THF or Chloroform.

compared to that of PM11Cz results in these phenomena. A focal-conic fan texture was observed above Tg of PM′11Cz. The X-ray diffraction pattern of the polymer displayed the strong diffraction peak in the small angle region at 2.2° corresponding to the layer spacing of 39.4 Å. The calculated value of the length of the side chain is about 36 Å. Therefore, mesomorphic phase structure of the polymer would be assigned to the smectic A_1 phase.

$PM11CzNO_2$, the polymethacrylate containing nitro-substituted carbazole, has Tg and T_{SmI} at 79°C and 214°C on heating process, respectively. ΔS_{SmI} for the polymer is $7.7 \times 10^{-3} JK^{-1}g^{-1}$. A focal-conic fan texture as shown in Figure 1b was observed in the mesomorphic temperature range and its texture was frozen below Tg on cooling process. This polymer shows the higher phase transition temperature and the wider mesomorphic temperature range than the polymethacrylate containing non-substituted carbazole, PM11Cz. This result indicates that the introduction of the nitro

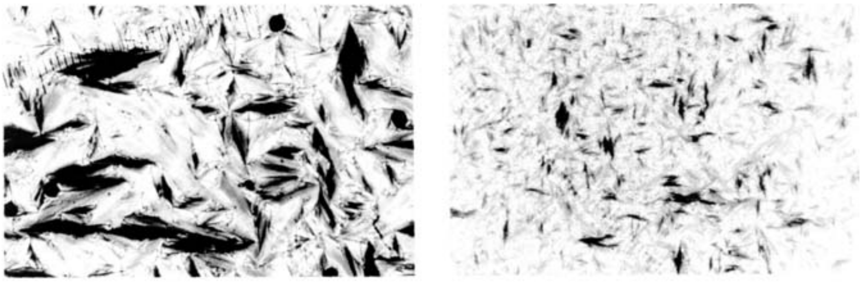

(a) (b)

FIGURE 1 Photomicrographs of polymethacrylate derivatives: (a) PM11Cz (170°C, cooling), (b) $PM11CzNO_2$ (180°C, cooling).

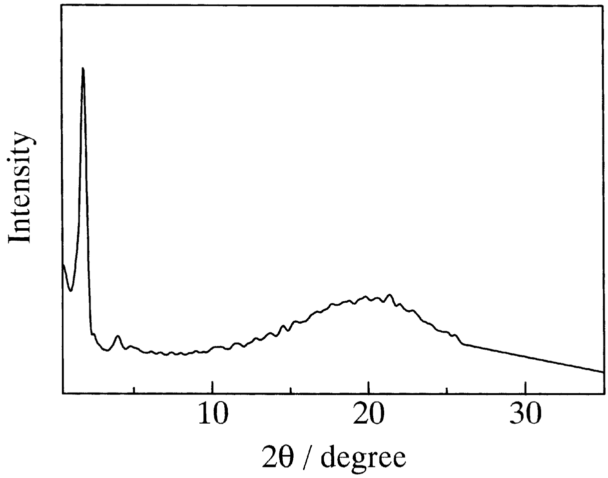


FIGURE 2 X-ray diffraction pattern of $PM11CzNO_2$.

group into the carbazolyl moiety enhances the thermal stability and stabilizes the LC phase.

One of the key points of $PM11CzNO_2$ is the small entropy change compared to PM11Cz. This result was related to the mesomorphic phase structure of polymers. The X-ray diffraction pattern (Fig. 2) of the polymer displayed the strong diffraction peak in the small angle region at 1.9° corresponding to the layer spacing of 46.5 Å and unassigned weak diffraction peak in the small angle region at 4.0°. The calculated value of the length of the side chain is about 33 Å. The experimental value is the 1.4 times larger than the calculated one, so LC phase of the polymer would be assigned to the smectic A_d phase. This result means that the nitro group affects the phase structure of polymers. The phase structure of the polymer would be affected by the interaction of nitro groups.

Polyester Derivatives (PmN12Cz)

Thermal properties of polyester derivatives are shown in Table III. P4N12Cz has Tg at 74°C on heating process. This polymer does not exhibit a mesophase.

P6N12Cz has Tg and T_{MI} (mesophase - isotropic phase transition temperature) at 60°C and 68°C, respectively. Birefringence as shown in Figure 3 was observed in the temperature range between Tg and T_{MI} of P6N12Cz. However, it is not a typical texture in the LC phase. The X-ray diffraction pattern of the polymer displayed the broad peak in the wide-angle region.

TABLE III Molecular Weights and Thermal Properties of Polyester Derivatives

Polymer	Molecular weight (Mn)	Phase transition temperature (°C)	$\Delta S_{MI}(JK^{-1}g^{-1})^{1)}$
P4N12Cz	—2)	$g \underset{?}{\overset{74}{\rightleftarrows}} I$	———
P6N12Cz	—2)	$g \underset{?}{\overset{60}{\rightleftarrows}} M \underset{?}{\overset{68}{\rightleftarrows}} I$	———
P8N12Cz	—2)	$g \underset{?}{\overset{56}{\rightleftarrows}} M \underset{?}{\overset{63}{\rightleftarrows}} I$	———

g: glassy, M: mesophase, I: isotropic phase.

1) Mesophase - isotropic phase transition entropy change.

2) Peak was not detected by GPC.

P8N12Cz has Tg and T_{MI} at 56°C and 63°C, respectively. Birefringence was observed in the temperature range between Tg and T_{MI} of P8N12Cz. The texture of P8N12Cz is similar to that of P6N12Cz, as shown in Figure 3. The mesomorphic temperature range of these polymers is very narrow. It is considered that the methylene units of polymer backbone would prevent the appearance of liquid crystallinity.

Polysiloxane Derivatives (PSiO11Cz, PSiC11Cz)

Thermal properties of polysiloxane derivatives are shown in Table IV. PSiO11Cz has Tg and T_{SmI} at 30°C and 209°C on the heating process,

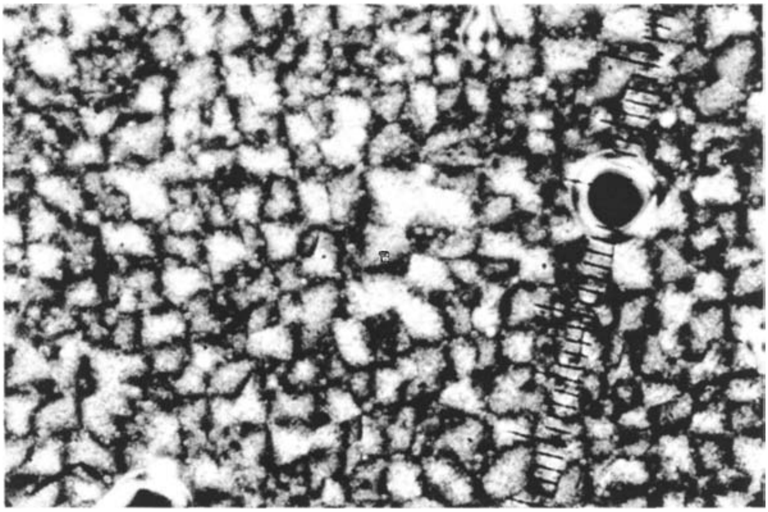


FIGURE 3 Photomicrograph of P6N12Cz (56°C, cooling).

TABLE IV Molecular Weights and Thermal Properties of Polysiloxane Derivatives

Polymer	Molecular weight (Mn)	Phase transition temperature (°C)	$\Delta S_{SmI}(JK^{-1}g^{-1})$1)
PSiO11Cz	8,400	$\underset{\xleftarrow[\qquad 23 \qquad]{}}{\mathrm{g} \xrightarrow{30} \mathrm{Sm1} \xrightarrow{79} \mathrm{M} \xrightarrow{102}} \mathrm{Sm2} \underset{207}{\overset{209}{\rightleftarrows}} \mathrm{I}$	2.3×10^{-2}
PSiC11Cz	—2)	$\mathrm{g} \underset{27}{\overset{32}{\rightleftarrows}} \mathrm{Sm} \underset{206}{\overset{208}{\rightleftarrows}} \mathrm{I}$	2.2×10^{-2}

g: glassy, Sm: smectic phase, M: mesophase, I: isotropic phase.

1) Smectic - isotrophic phase transition entropy change.

2) Peak was not detected by GPC.

respectively. Whereas only two transition temperatures, 207°C and 23°C were detected on the cooling run. Furthermore, the exothermic transition and endothermic transition were exhibited at 79°C and 102°C, respectively. These enthalpy changes and the X-ray diffraction patterns at the temperatures exhibited these phases are almost the same. Therefore, the liquid crystal phase would be unstable in the temperature range between 79°C and 102°C.

A focal-conic fan texture as shown in Figure 4a was observed in the mesomorphic temperature range, and its texture was frozen below Tg of PSiO11Cz on the cooling process. The X-ray diffraction pattern of the polymer displayed the strong diffraction peak in the small angle at 2.6° corresponding to the layer spacing of 34.0 Å. It also displayed the 2nd diffraction peak at 5.2°. Furthermore a weak diffraction peak was also detected at 11.0° in the X-ray diffraction pattern, however the assignment of the peak was not clarified. The calculated value of the length of the side

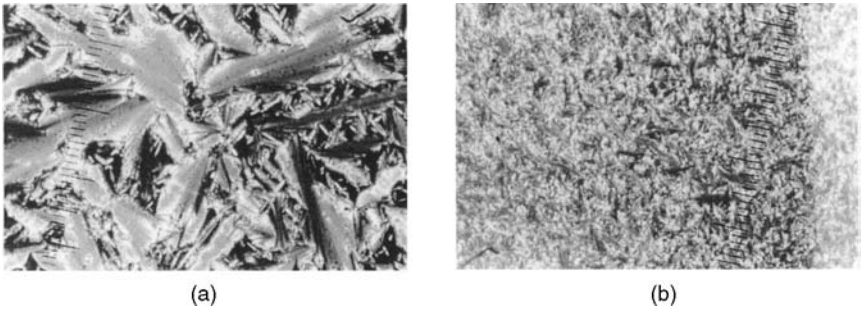

(a) (b)

FIGURE 4 Photomicrographs of Polysiloxane derivatives: (a) PsiO11Cz (202°C, cooling), (b) PsiC11Cz (198°C, cooling).

TABLE V Molecular Weights and Thermal Properties of Polymaleimide Derivatives

Ploymer	Molecular weight (Mn)	Phase transition temperature (°C)	$\Delta S_{MI}(JK^{-1}g^{-1})^{1)}$
PMI10Cz	7,000	$\mathrm{g}\underset{72}{\overset{72}{\rightleftarrows}}\mathrm{Sm1}\underset{122}{\overset{127}{\rightleftarrows}}\mathrm{Sm2}\underset{189}{\overset{192}{\rightleftarrows}}\mathrm{I}$	1.1×10^{-2}
PMI5Cz	4,800	$\mathrm{g}\underset{96}{\overset{103}{\rightleftarrows}}\mathrm{N}\underset{189}{\overset{190}{\rightleftarrows}}\mathrm{I}$	1.2×10^{-3}

g: glassy, Sm: smectic phase, N: nematic phase, I: isotrophic phase.

1) Smectic or nematic - isotrophic phase transition entropy change.

chain is about 34 Å. Therefore, mesomorphic phase structure of the polymer would be assigned to the smectic A_1 phase.

PSiC11Cz has Tg and T_{SmI} at 32°C and 208°C on the heating process, respectively. However, this polymer does not show the exothermic or endothermic transition exhibited by PSiO11Cz. The result means that siloxane ring would contribute the stability of the LC phase. A focal conic-fan texture as shown in Figure 4b was observed in the mesomorphic temperature range and its texture was frozen below Tg of PSiC11Cz on cooling process. The mesomorphic phase structure of this polymer would also be assigned to the smectic A_1 phase by the X-ray diffraction measurement.

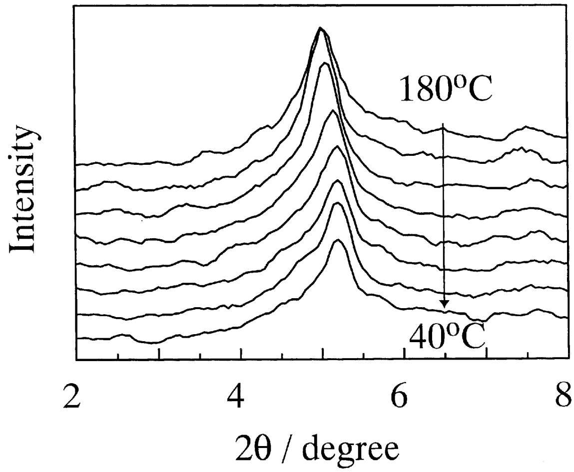


FIGURE 5 X-ray diffraction patterns of PMI10Cz (180, 160, 140, 120, 100, 80, 60, and 40°C).

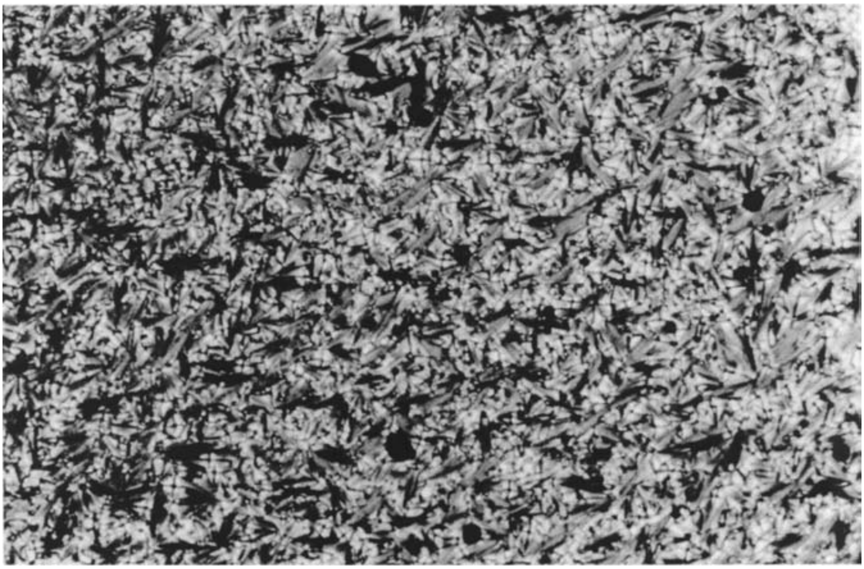


FIGURE 6 Photomicrograph of PMI10Cz (150°C, cooling).

Polymaleimide Derivatives (PMI10Cz, PMI5Cz)

Thermal properties of polymaleimide derivatives are shown in Table V. PMI10Cz has Tg and T_{MI} (nematic or smectic phase - isotropic phase transition temperature) at 72°C and 192°C on the heating process, respectively.

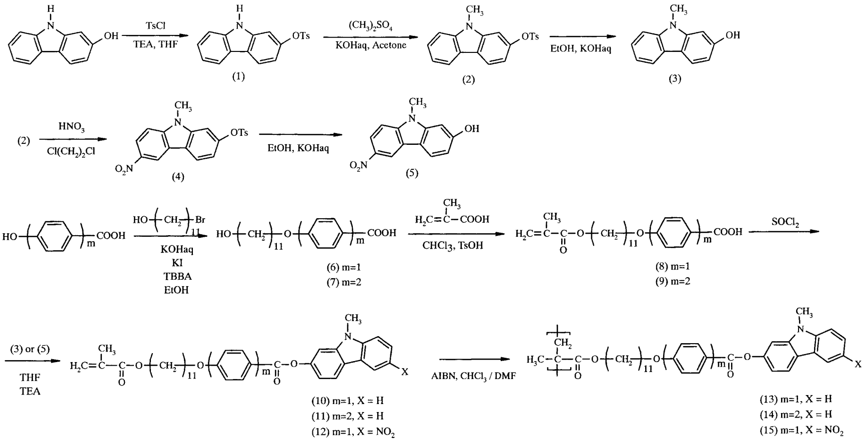


FIGURE 7 Synthesis of polymers.

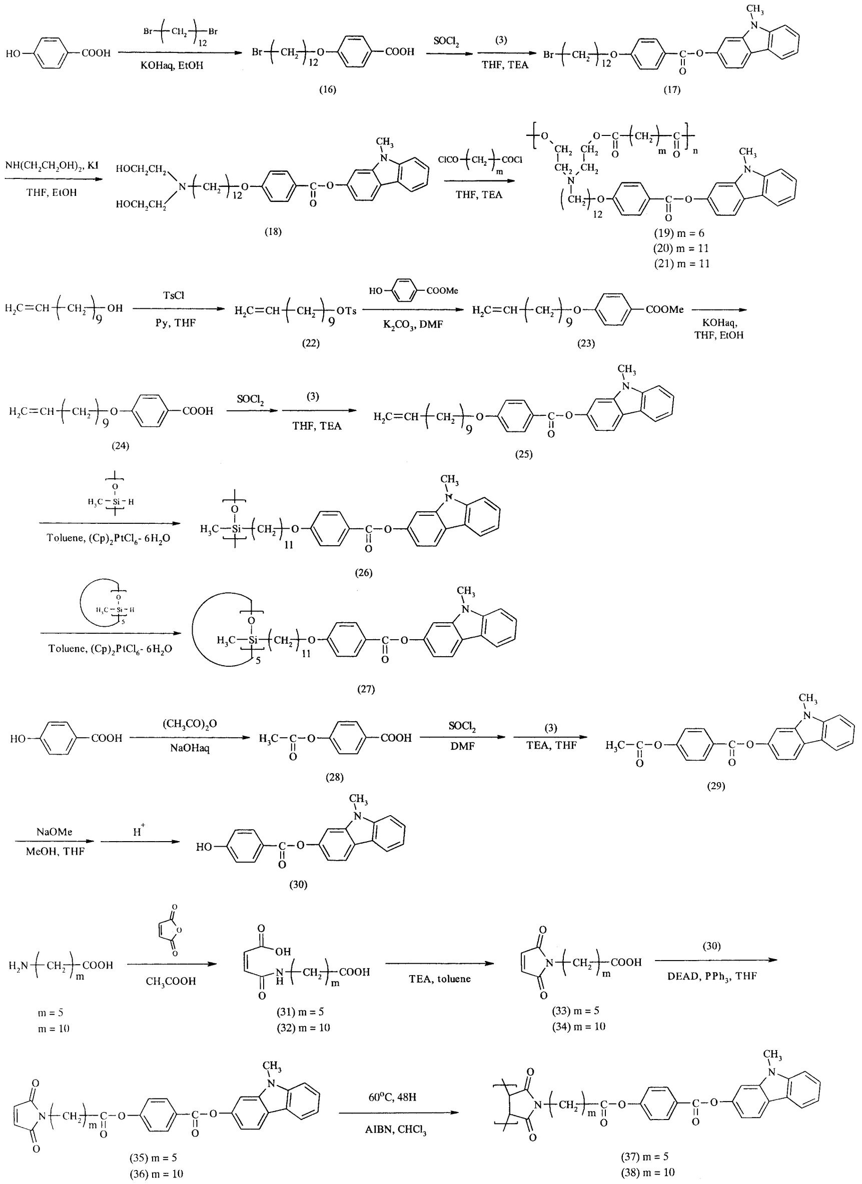


FIGURE 8 Synthesis of polymers.

Furthermore, endothermic transition was exhibited at 127°C. This transition was also confirmed on the cooling process. Therefore, PMI10Cz exhibited two mesomorphic phases. The temperature dependence of X-ray diffraction measurement as shown in Figure 5 also supports these results. Focal-conic fan textures as shown in Figure 6 were observed in both the mesomorphic temperature ranges.

The X-ray diffraction pattern of the polymer in the higher mesomorphic temperature displayed the strong reflection at 5.0° corresponding to the layer spacing of 17.7 Å. The calculated value of the length of the side chain is about 29 Å. Therefore, LC phase of the polymer would be assigned to the smectic C phase. The tilt angle is about 52°. On the other hand, the tilt angle of the mesomorphic phase in the lower temperature is about 54°.

It is known that polymaleimides have higher Tg. However, Tg of the synthesized polymer, PMI10Cz, is not as high as the other synthesized polymer, such as the polymethacrylate derivatives. To examine the relationship between Tg and the methylene unit in the side chain, we synthesized PMI5Cz. It has Tg at 103°C on heating process, so the short methylene unit in the side chain led to the high Tg. However, its ΔS_{MI} is $1.2 \times 10^{-3} JK^{-1}g^{-1}$. This value is about one order smaller than of the ΔS_{MI} exhibited by PMI10Cz. Therefore, the mesomorphic phase of PMI5Cz would be assigned to the nematic phase.

EXPERIMENTAL

Characterization

^{1}H-NMR spectra were obtained by JNM-LA400 and JNM-LA500 spectrometer using $CDCl_3$ or DMSO as a solvent. Infrared (IR) spectra were taken on JEOL JIR7000 type spectrometer. DSC measurements were conducted with Mettler DSC821^e. Heating and cooling rates were 5°C/min in all cases. Optical microscopy was performed on a Nikon polarizing optical microscopy, OPTIPHOTO-POL, equipped with a Mettler FP80 controller and a FP82 hot stage. X-ray diffraction patterns were recorded with a RIGAKU RINT 2500 series. The samples in quartz capillaries were held in a temperature-controlled cell. Molecular weight of polymers is obtained by TOSO HLC-8020 GPC system. Polystyrene is used as the standard material.

Synthesis

Figure 7 and 8 show the synthesis of the polymers [13].

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