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SHORT COMMUNICATION

Synthesis of a side chain liquid crystalline polymer containing the cholesteryl moiety via ROP and “click” chemistry

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Abstract Propargyl monocholesterylsuccinate (ChPS) was prepared through the esterification of monocholesterylsuccinate with propargyl alcohol, and poly(3-azidomethyl-3-methyloxetane) (PAMMO) was synthesized via cationic polymerization, using boron trifluoride etherate as catalyst and benzyl alcohol as initiator in methylene chloride. Through the copper-catalyzed “click” reaction between the azide group on PAMMO and the alkyne group on ChPS, a side chain liquid crystalline polymer containing the cholesteryl moiety (Ch-SCLCP) was obtained. The “click” reaction was confirmed by IR, ^{1}H NMR, ^{13}C NMR, and GPC studies. The resulting polymer showed thermotropic mesophase as judged by polarized optical microscopy (POM) and differential scanning calorimetry (DSC).

Keywords “click” chemistry · Ring-opening polymerization (ROP) · Side chain liquid crystalline polymer

Introduction

Liquid crystalline polymers (LCPs) offer the advantageous combination of the anisotropy of liquid crystals with the attractive bulk properties and processing possibilities of polymers. As one type of the LCPs, side chain liquid crystalline polymers (SCLCPs) are of special interest to the study due to their potential application in numerous areas, for instance, in the field of data storage systems, nonlinear optical systems, pyro-, piezo-, and ferroelectric devices [1–3]. To date, most of the side chain liquid crystalline polymers are prepared via polymerization of the corresponding liquid crystalline monomers [4–8]. However, synthesis and purification of the liquid crystalline monomers are rather tedious for researchers.

In the past few years, “click” reactions, as termed by Sharpless et al. [9], have gained a great deal of attention due to their high specificity, quantitative yields, and near-perfect fidelity in the presence of most functional groups. The most popular “click” chemistry reaction is the Huisgen dipolar cycloaddition reaction between an azide and an alkyne, leading to 1,2,3-triazole [10–12]. The great potential of this coupling procedure for the construction of well-defined (functional) polymers [13–19], bioconjugated polymers [20, 21], and polymers with complex topologies [22–27] has been quickly recognized and is the subject of intensive research.

We describe, herein, the first synthesis of a side chain liquid crystalline polymer containing the cholesteryl moiety (Ch-SCLCP) by combining the ring-opening polymerization (ROP) and “click” chemistry and the characterization of the resulting polymer.

Experimental

Caution: owing to the high explosive characteristics and toxicity of compounds bearing azide group, they should be handled with care in very small amounts, and all reactions with these compounds must be conducted in a well-designed hood, using a safety shield or barrier to protect against possible explosion. Appropriate impermeable gloves and splash goggles should be worn at all times to prevent skin and eye contact, always wear full-length

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pants and closed-toe shoes. In addition, the reaction waste must be placed in a separate, explicitly-labeled container designated solely for azide waste. Extra caution must be taken to make certain that azide waste not come in contact with acid.

Materials

Propargyl alcohol (99%) was used as received from Acros Organics. THF, DMF, dichloromethane, benzene, and toluene were purchased from Tianjin Kewei Ltd and distilled from CaH_2. Boron trifluoride dietherate (reagent grade, Tianjin Keruisi Ltd.) was distilled just prior to use. Sodium azide was used as received from Tianjin Kewei Ltd. Benzyl alcohol from Tianjin Keruisi Ltd. was distilled under vacuum before use. Monocholesterylsuccinate was prepared according to a procedure described by Shaikh et al. [28], and its structure was confirmed via ^{1}H NMR. 3-Methyl-3-(toluenesulfonyloxymethyl)oxetane was prepared according to a method described in the literature [29]. $(PPh_3)_3CuBr$ was synthesized from published procedure [30]. All other chemicals were purified according to conventional methods or used as received.

Characterization

^{1}H NMR (400 MHz) spectra were recorded at room temperature on a Varian-400 spectrometer. $CDCl_3$ was used as the solvent. The chemical shifts were referenced relative to the solvent. IR spectra were recorded on a Bio-Rad FTS-135 spectrometer. The spectral resolution was maintained at 2 cm^{-1}. Molecular weights and molecular weight distributions were measured with a Waters 1515 gel permeation chromatograph (GPC) equipped with a Waters 2410 differential refractometer as detector. Three Styragel columns (HR2, HR4, HR6) were used in series. GPC samples were run at 40 °C with THF as the mobile phase at a flow rate of 1 mL/min, and the columns were calibrated using narrow distribution polystyrene standards obtained from Polymer Laboratories Ltd. UK. The phase transition temperature of the polymer was determined with a NETZSCH DSC204 calorimeter under nitrogen atmosphere, at the heating and cooling rates of 10 °C/min. High purity indium and zinc were used to calibrate the calorimeter. The thermogravimetric analysis (TGA) was performed on a NETZSCH TG209 instrument, using nitrogen as purge gas, operating from 20 to 600 °C with a heating rate of 10 °C /min. Polarized optical microscopy (POM) was performed on an Olympus BX51M microscope fitted with a Linkam TH600 hot stage and a LinkamTMS94 thermal controller. To obtain micrographs, a powder sample was placed between two glass plates.

Synthesis of propargyl monocholesterylsuccinate

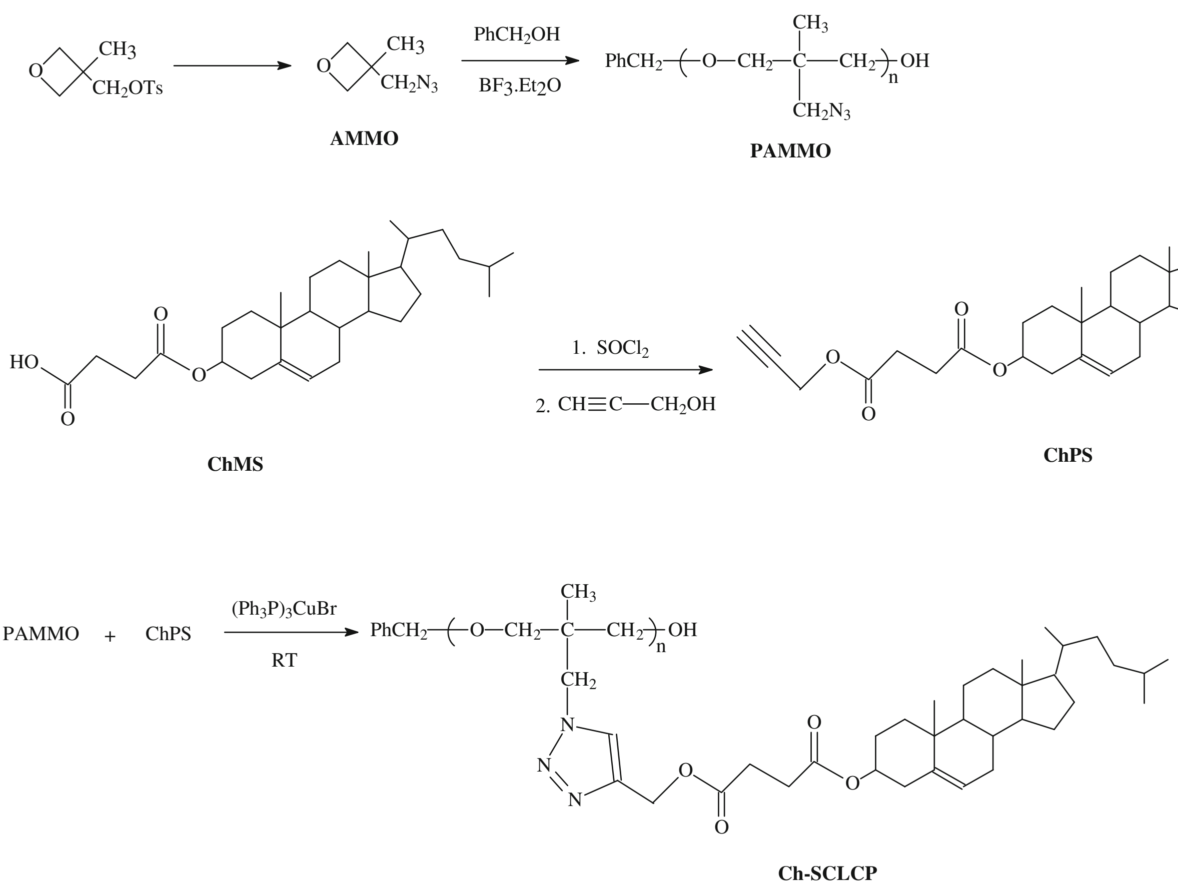
A 100 mL flask with a stir bar was charged with monocholesterylsuccinate (9.2 g, 19 mmol), thionyl chloride (10 mL) and dry tetrahydrofuran (THF; 40 mL). The reaction mixture was stirred at room temperature for 24 h. At the end of reaction time, the solvent and excess thionyl chloride were removed under reduced pressure. Dry benzene (15 mL) was added, and the reaction mixture was stirred for 10 min. The benzene was then removed under reduced pressure. Addition and removal of benzene was repeated three times to ensure complete removal of thionyl chloride. The product was then dissolved in 30 mL of dry toluene, and the solution was slowly added to another flask containing propargyl alcohol (2.5 mL, 42 mmol), triethylamine (4.0 mL, 28 mmol) and toluene (30 mL) under an argon atmosphere in an iced bath and then stirred for 24 h at room temperature. The reaction mixture was washed with 5% $NaHCO_3$, saturated NaCl, and water, dried over Na_2SO_4, and concentrated in vacuum. The residual solid was purified by twice recrystallization from ethanol, giving propargyl monocholesterylsuccinate (ChPS) as a white solid (mp: 101–102 °C, yield: 68%).

^{1}H NMR ($CDCl_3$) 5.35 (m, 1H, =CH), 4.70 (m, 2H, ≡C–CH_2O), 4.62 (m, 1H, O–CH–), 2.65 (t, 4H, O=C–CH_2CH_2C=O), 2.48 (m, 1H, ≡CH), 2.30–0.67 (m, 43H, cholesteryl). ^{13}C NMR ($CDCl_3$): 171.5, 171.3, 139.6, 122.7, 77.5, 74.9, 74.4, 56.7, 56.2, 52.1, 50.0, 42.3, 39.8, 39.5, 38.0, 37.0, 36.6, 36.2, 35.8, 31.9, 29.3, 29.0, 28.2, 28.0, 27.7, 24.3, 23.9, 22.8, 22.6, 21.0, 19.3, 18.7, 11.8. IR (KBr, cm^{-1}): 3,260 (≡C–H); 2, 120 (C≡C); 1,730 (–C=O).

Synthesis of 3-azidomethyl-3-methyloxetane

3-azidomethyl-3-methyloxetane (AMMO) was prepared through the reaction of 3-methyl-3-(toluenesulfonyloxymethyl)oxetane with sodium azide in DMF or water.

Process I [31] In a reaction flask with a stir bar, 3-methyl-3-(toluenesulfonyloxymethyl)oxetane (12.9 g, 50 mmol) and sodium azide (3.6 g, 55 mmol) were suspended in DMF (25 mL). The flask was heated at 85 °C in an oil bath for 24 h, after which the mixture was cooled to ambient temperature, poured into water (100 mL), and extracted with methylene chloride (3×15 mL). The organic phase was dried over anhydrous Na_2SO_4, and concentrated. The resultant pale yellow oil was distilled to give 4.6 g (yield: 72%) of colorless liquid: bp 45–47 °C/532 Pa (caution: do not over heat).



Scheme 1 Reaction scheme for the preparation of PAMMO, ChPS, and the subsequent copper(I)-catalyzed "click" reaction

Process II A reaction flask with a stir bar was loaded with a mixture of 3-methyl-3-(toluenesulfonyloxymethyl)oxetane (7.8 g, 30 mmol), tetra-*n*-butylammonium bromide (0.2 g, 0.6 mmol), sodium azide (2.1 g, 32 mmol), and water (10 mL). The flask was then heated at about 96 °C to about 105 °C in an oil bath for 6 h, after which the mixture was cooled to ambient temperature, and extracted twice with methylene chloride (10 mL). The organic extract was passed through a column containing aluminum oxide and dried over Na_2SO_4. The solvent was then evaporated to give 3.5 g (yield: 91%) of AMMO.

^1H NMR ($CDCl_3$) 4.35–4.45 (m, 4H,–CH_2–O), 3.53 (s, 2H,–CH_2N_3), 1.33 (s, 3H,–CH_3).

Synthesis of poly(3-azidomethyl-3-methyloxetane) (PAMMO)

Cationic ring-opening polymerization was employed using boron trifluoride dietherate and benzyl alcohol as catalyst and initiator, respectively. A round-bottomed flask with a stir bar, thermometer, argon inlet/outlet and serum cap, was cooled from 120 °C to ambient temperature under a stream of argon. The flask was then connected to a cooling circulator and charged with benzyl alcohol (52 μL, 0.5 mmol) and methylene chloride (2 mL). The reactor was cooled under argon to 0 °C and boron trifluoride dietherate (63.4 μL, 0.5 mmol) was added. The mixture was stirred for 45 min and then a solution of 3-azidomethyl-3-methyloxetane (AMMO; 2.5 g, 20 mmol) in dichloromethane (4 mL) was pumped into

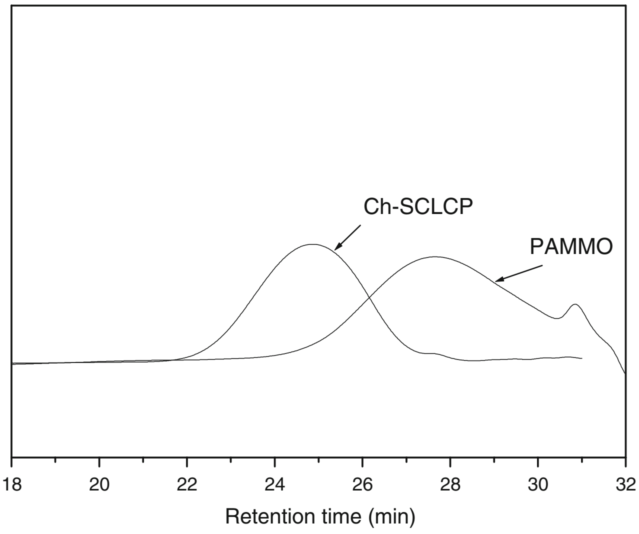


Fig. 1 GPC curves of PAMMO and the coupling product Ch-SCLCP

the flask over a period of 4 h. The reaction was kept at 0 °C for another 4 h with stirring. The reaction mixture was then brought to room temperature and quenched with 10 mL of 5% $NaHCO_3$ solution. The mixture was extracted twice with 10 mL of methylene chloride, dried over Na_2SO_4, and evaporated to dryness (yield, 79%).

GPC M_n=3,490 g/mol; M_w/M_n=1.53. ^1H NMR ($CDCl_3$): 3.05–3.20 (m, 6H, $–CH_2–O$, and $–CH_2N_3$), 0.94 (s, 3H, $–CH_3$). ^{13}C NMR ($CDCl_3$): 74.1 ($CH_2–O$), 55.6 ($–CH_2N_3$), 41.5 (quaternary C), 18.1 ($–CH_3$).

Safety note AMMO and PAMMO are potentially-explosive, energy-rich substances of moderate to considerable sensitivity to initiation by heat, light, pressure, impact, shock, friction, and other means. It should be stored below room temperature (−18 °C) and in the dark.

Synthesis of Ch-SCLCP via "clicking" of ChPS to PAMMO

A solution of PAMMO (0.19 g, 1.5 mmol of "clickable" azide units), ChPS (1.18 g, 2.25 mmol) and triethylamine (0.11 mL, 0.75 mmol) in THF (15 mL) was degassed by bubbling argon for 20 min. $(PPh_3)_3CuBr$ (0.14 g, 0.15 mmol) was then added and argon was bubbled into the resulting solution for a further 10 min. The reaction solution was stirred at ambient temperature for 3 days and then passed through a short neutral alumina column eluting with THF. The resulting solution was concentrated under reduced pressure and precipitated into ethyl acetate (100 mL). The solid was separated by centrifugation (yield: 87%). GPC: M_n=14,330 g/mol; M_w/M_n=1.32.

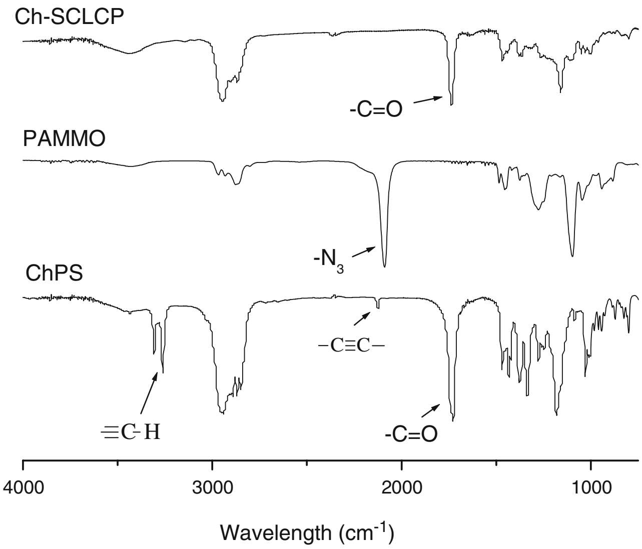


Fig. 2 IR transmission spectra of PAMMO, ChPS, and the coupling product Ch-SCLCP

Results and discussion

A side chain liquid crystalline polymer containing the Ch-SCLCP was prepared as outlined in Scheme 1.

Nucleophilic substitution reaction with azide group can be carried out in either organic solvent or water [32–36]. In this study, two processes have been taken for the preparation of 3-azidomethyl-3-methyloxetane (AMMO) through the reaction of 3-methyl-3-(toluenesulfonyloxy-methyl)oxetane with sodium azide. One reaction was performed in DMF, and the other was in water along with a phase transfer catalyst, tetra-*n*-butylammonium bromide (TBAB). Sodium azide and the resulting AMMO possess

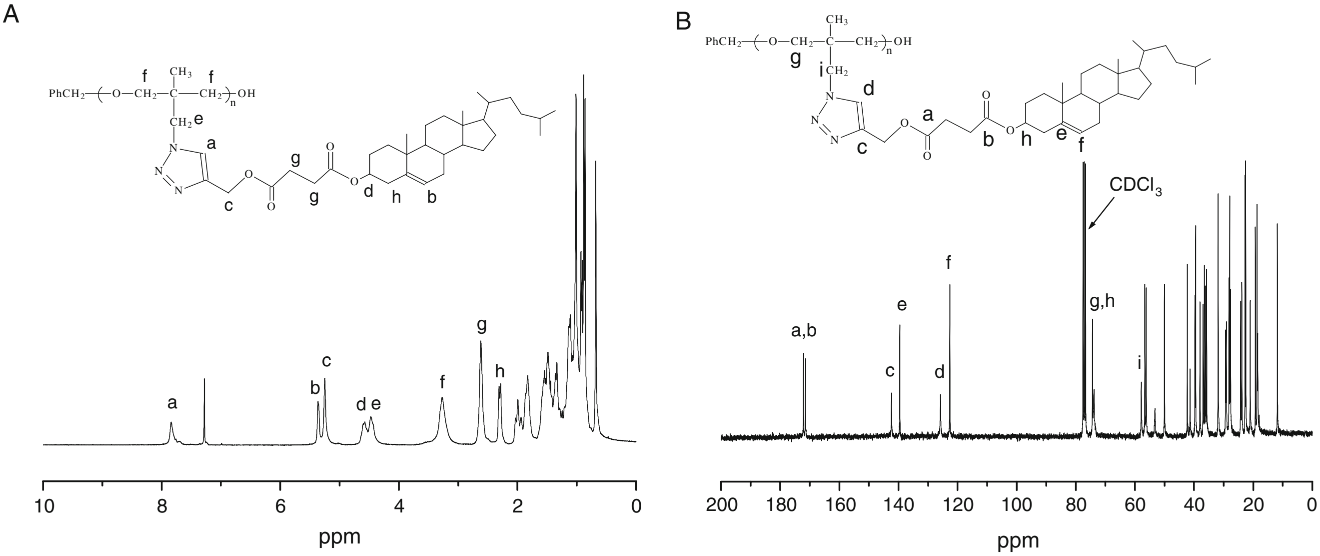


Fig. 3 ^1H NMR (**a**) and ^{13}C NMR (**b**) spectra of the coupling product Ch-SCLCP

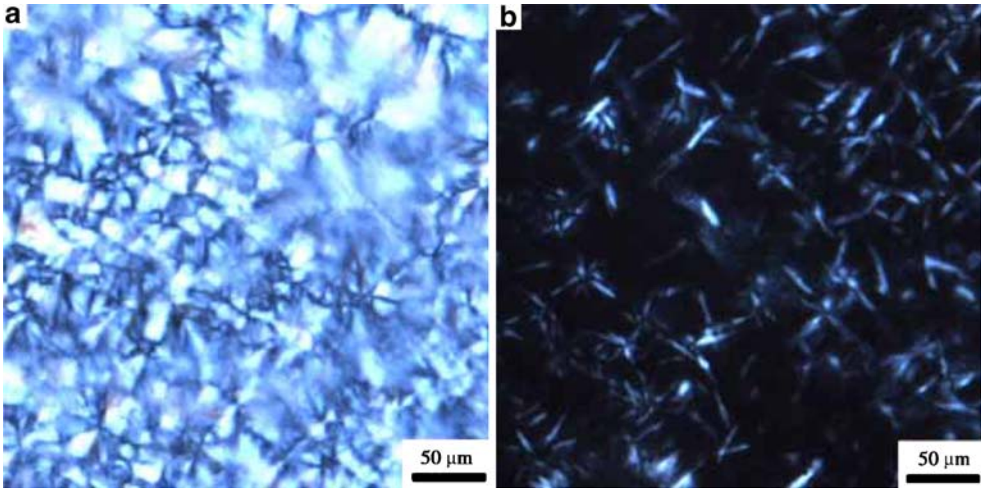


Fig. 4 Representative polarized optical micrographs of Ch-SCLCP. **a** At 280.0 °C on the first heating scan; **b** at 283.6 °C on the first cooling scan

positive heat of formation and, thus, the aqueous process was relatively safe since it was conducted at reflux of water, which removed heat from reaction, thereby, avoiding exothermic and run away reactions. Cationic polymerization was employed to synthesize PAMMO, using boron trifluoride etherate as catalyst and benzyl alcohol as initiator in methylene chloride at 0 °C. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n), measured by GPC in THF, were 3,490 g/mol and 1.53, respectively. Relatively high polydispersity of the obtained PAMMO could be attributed to the formation of cyclic oligomers, indicated by the appearance of a low molecular weight shoulder in the molecular weight distribution [37]. Thermogravimetric analysis (TGA) of PAMMO showed that the weight loss reached 5.0% at 231.0 °C. Afterwards, PAMMO decomposed rapidly. The degree of weight loss showed a steep increase, and the weight loss reached 89.6% at 246.0 °C. ChPS was prepared through the esterification of monocholesterylsuccinate with propargyl alcohol and its structure was confirmed by ^{1}H NMR with the appearance of the C≡CH signal at 2.5 ppm, ^{13}C NMR with the acetylene carbons resonate at 77.5 and 74.9 ppm, and IR analysis with the alkyne C–H stretching frequency at 3,260 cm^{-1}, C≡C signal at 2,130 cm^{-1}.

The coupling reaction between ChPS and PAMMO (M_n= 3,490 g/mol; M_w/M_n=1.53) with a molar ratio of alkyne group to azide group of 1.5:1, was conducted in THF, with $(PPh_3)_3CuBr$ as the catalyst, in the presence of triethylamine (TEA). As shown in Fig. 1, the number-average molecular weight and the molecular weight distribution of the coupling product Ch-SCLCP were 14,330 g/mol and 1.32, respectively, as evaluated with GPC. The change of molecular weight is a clear indication of the efficient "click" reaction. Decrease of the shoulder peak in the GPC curve of the coupling

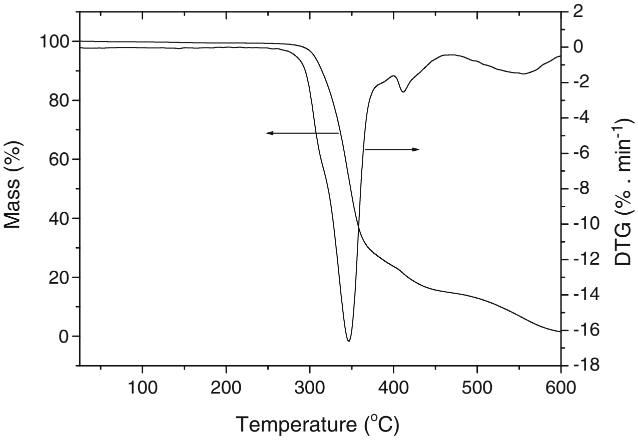


Fig. 5 Thermogravimetric (*TG*) and derivative thermogravimetric (*DTG*) curves of the coupling product Ch-SCLCP

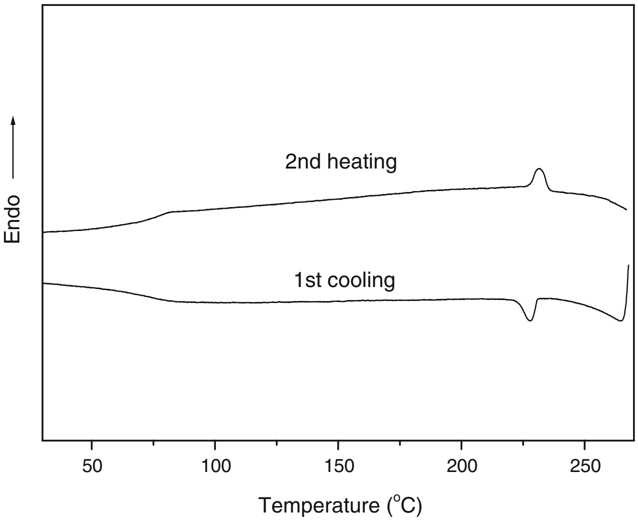


Fig. 6 DSC thermograms of Ch-SCLCP in the first cooling and the second heating mode (10 °C/min, the upper limit of temperature was set as 270 °C)

product and the significant change of the molecular weight distribution were attributed to purification of Ch-SCLCP by precipitation with ethyl acetate, resulting in the removal of low molecular weight parts produced by coupling reaction between ChPS and cyclic oligomers. IR, ^{1}H NMR, and ^{13}C NMR analyses also confirmed that the coupling reaction between ChPS and PAMMO was very efficient. As shown in Fig. 2, the absorption at 2,102 cm^{-1}, typical of the azide groups disappeared completely. ^{1}H NMR analysis (Fig. 3a) clearly indicated the disappearance of the peak at 2.5 ppm assigned to the C≡CH signal and the appearance of a new peak at 7.9 ppm assigned to the proton of triazole. The ^{13}C NMR spectrum (Fig. 3b) of Ch-SCLCP acquired in $CDCl_3$ shows peaks at 172.2 and 171.5 ppm for the carbons of the carbonyl moiety. Olefin carbons of the cholesteryl group were noticed at 139.6 and 122.7 ppm. Furthermore, olefin carbons of the triazole ring were observed at 142.4 (quaternary) and 125.8 ppm in accordance with the assigned structure.

In order to investigate the thermotropic properties of the coupling product Ch-SCLCP, we performed polarized optical microscopic observation of the sample sandwiched between two glass plates as the temperature was changed. When it was heated at a rate of 10 °C/min, the sample melted at 243.3 °C. Above this point, we observed a liquid crystalline texture (Fig. 4a), which was transformed into the dark-field view at 299.9 °C. Upon cooling, the birefringence appeared, and a needle form (Fig. 4b) was seen in the crystals. To support this finding, the coupling product Ch-SCLCP was investigated by means of differential scanning calorimetry (DSC). However, DSC investigation of Ch-SCLCP proved to be difficult due to the thermal instability of this polymer. Upon heating, Ch-SCLCP decomposed exothermally above ca. 270 °C. Thermogravimetric analysis (TGA) of Ch-SCLCP (Fig. 5) showed that the weight loss reached 4.5% at 305 °C. Therefore, mesomorphic-to-isotropic transition of Ch-SCLCP was covered by the exothermic peak, and the clear point (T_i) can not be detected from the DSC curve. Similar observations have been reported by other researchers [38–40]. Figure 6 shows the representative DSC traces in the cooling and second heating scans when the upper limit of temperature was set as 270 °C. It can be seen that the glass transition at 72.2 °C and melting temperature (T_m) at 231.4 °C can easily be detected from the second heating scan. In general, the phase behavior of side chain LCPs depends on the nature of the polymer backbone, the length of the mesomorphic core, and flexibility. The mesomorphic cores are usually attached to the polymer backbone through the flexible spacer. The melting temperature and the clear point decreased with increased length of the flexible spacer. In this study, the high melting temperature and high clear point resulted from the low flexibility of the side chain.

Conclusion

PAMMO bearing side azide group was synthesized via cationic polymerization. Through the copper-catalyzed “click” reaction between the azide group on PAMMO and the alkyne group on ChPS, a side chain liquid crystalline polymer containing the Ch-SCLCP was successfully prepared. The “click” reaction was confirmed by means of IR, ^{1}H NMR, ^{13}C NMR, and GPC. The resulting polymer showed thermotropic mesophase as judged by POM and DSC. Because of the advantages of the “click” reaction, the approach reported here provides a promising option to prepare side chain liquid crystalline polymers.

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