

# Synthesis of liquid crystalline block copolymer obtained by using main-chain polyurethane initiator and its thermal properties

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## Abstract

A novel main-chain polyurethane initiator was obtained by the ternary polyaddition of mesogenic diol, aliphatic azodiols (initiator component), and diisocyanate. The mesogenic diol, in which 6-hydroxyhexyloxy groups linked to both sides of azobenzene, was synthesized. Subsequently, the novel liquid crystalline block copolymer, which has a multiblock structure consisting of alternately linked main-chain polyurethane and polymethacrylate units, was obtained by the radical polymerization of a methacrylate monomer (M11) having benzoic acid as the end group using the main-chain polyurethane initiator. The main-chain polyurethane initiator formed a nematic phase on the heating and cooling processes. Furthermore, the homopolymethacrylate (HPM11) obtained from M11 exhibited a smectic A phase. The main-chain polyurethane initiator could not be miscible with HPM11, and the phase separation was formed. However, the liquid crystalline block copolymer uniformly exhibited the nematic phase on the heating and cooling processes.

## Key words

liquid crystal, polymer initiator, block copolymer, phase transition, nematic

## 1. Introduction

Polyurethanes have excellent elasticity and toughness, and by changing the formulation and molding method, various performances such as hydrophilicity, heat resistance, and chemical resistance can be achieved (Meier-Westhues et al., 2019). For this reason, its applications have been expanding in recent years, and novel developments in polyurethanes are expected. In general, the polyurethanes are synthesized by the polyaddition of polyols and diisocyanates. The polyaddition also is performed at temperature below room temperature. This polyaddition below room temperature is also effective for polymerization with heat-sensitive compounds. Main-chain polyurethanes with an azo radical polymerization initiator unit (AI) have been reported to be effective in the synthesis of block copolymers (Ueda et al., 1976; Furukawa et al., 1967; Kinoshita et al., 1993). On the other hand, the introduction of mesogenic groups as a structural unit in polyurethanes can lead to the formation of liquid crystalline phases (Padmavathy et al., 2003; Ujiie et al., 2015; 2017). It is also possible to introduce AI into liquid crystalline polyurethanes, which can be used to easily obtain liquid crystalline block copolymers consisting of main-chain and side-chain polymer units. This method can be used as a modification technique for liquid crystal polyurethanes. Furthermore, the block copolymerization, in which immiscible polymers are linked

together, is expected to lead to the formation of a liquid crystalline phase without phase separation of the polymer units. We synthesized novel polyurethane initiators and block copolymers to control the thermal properties and orientation of liquid crystalline polyurethanes. This paper describes the synthesis and phase transitions of the liquid crystalline block copolymer.

## 2. Experimentals

### 2.1 Materials

The synthetic route of the liquid crystalline block copolymer is shown in Figure 1. The polyurethane initiator (PUI) was synthesized by the ternary polyaddition of diisocyanate (TDI), azobisalcohol (azo initiator, ABA), and mesogenic diol (MD66) (Figure 2). ABA and TDI were purchased from Fujifilm Wako Pure Chemical Corporation and Tokyo Chemical Industry

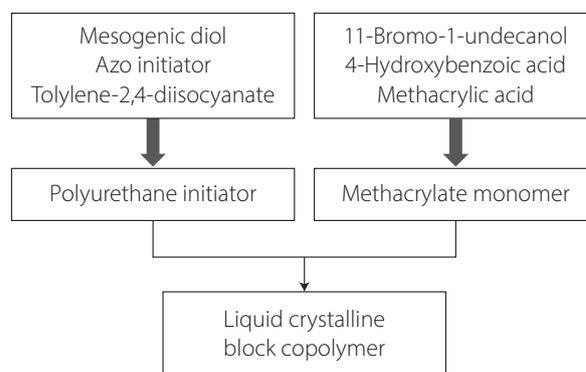


Figure 1: Synthetic route of liquid crystalline block copolymer

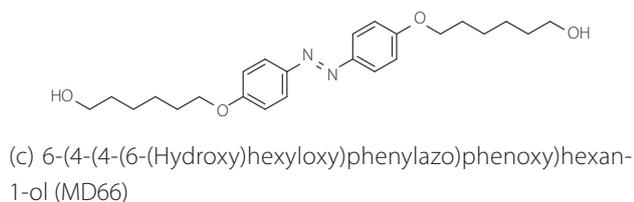
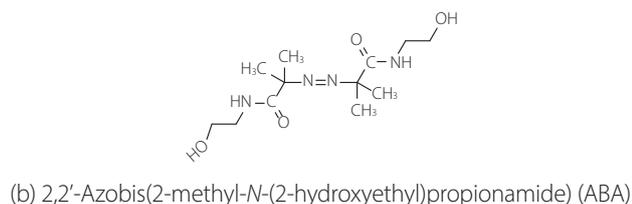
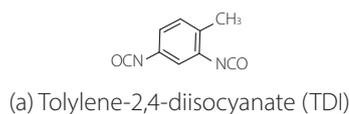


Figure 2: Structures of tolylene-2,4-diisocyanate (TDI), azo initiator (ABA), and mesogenic diol (MD66)

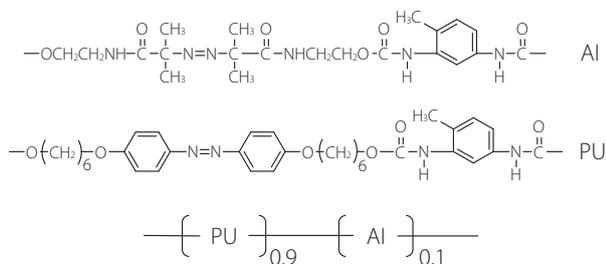


Figure 3: Structure of main-chain polyurethane initiator (PUI, random copolymer)

Note: The molar fractions of PU and AI units were estimated by  $^1\text{H}$  NMR measurement.

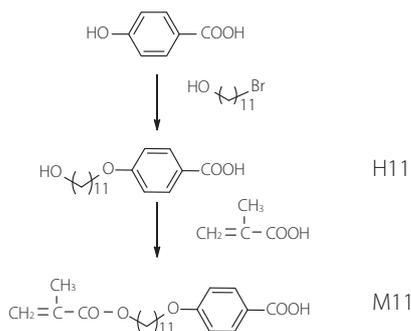


Figure 4: Synthetic scheme of methacrylate monomer (M11) with benzoic acid unit

Co., Ltd., respectively. MD66 was synthesized by modifying a method described in the literature (Ujii et al., 2015). A block copolymer was synthesized by the solution radical polymerization of a methacrylate monomer (M11) using PUI as the initiator. The synthetic scheme of M11 was shown in Figure 4. The structure of the block copolymer was exhibited in Figure 5.

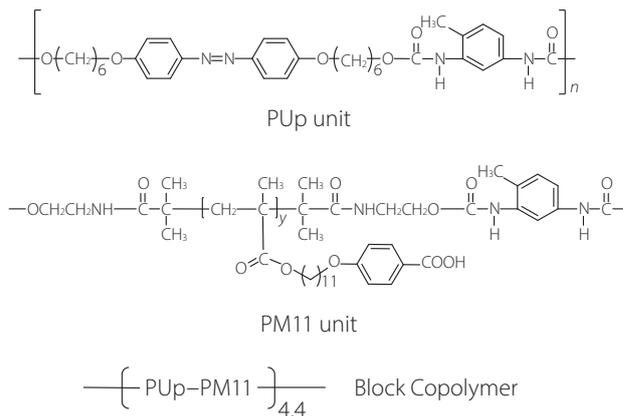


Figure 5: Structure of liquid crystalline block copolymer (PUI-PM11)

## 2.2 Synthetic methods

### 2.2.1 Polyurethane initiator (PUI)

ABA, TDI, and dibutyltin (IV) dilaurate were dissolved in tetrahydrofuran (THF) at room temperature, and the solution was stirred. After 24 h, MD66 was added to the THF solution and stirred for 48 h. After the reaction, the THF solution was evaporated, and PUI (Figure 3) dried under reduced pressure.

### 2.2.2 Methacrylate monomer (M11)

11-Bromoundecanol, 4-hydroxybenzoic acid, and potassium hydroxide were dissolved in ethanol, and the ethanol solution was refluxed at  $80\text{ }^\circ\text{C}$  for 24 h. After the reaction, the ethanol solution was evaporated, and the crude product was dissolved in water. The water solution was neutralized with hydrochloric acid, and the precipitation (H11) was filtered off. H11, methacrylic acid, hydroquinone, and *p*-toluenesulfonic acid were dissolved in chloroform and refluxed for 24 h. After the chloroform solution was washed with water, the chloroform solution was dried with magnesium sulfate. The chloroform solution was evaporated, and M11 (Figure 4) was dried under reduced pressure.

### 2.2.3 Block copolymer (PUI-PM11)

PUI and M11 were dissolved in THF and polymerized at  $55\text{ }^\circ\text{C}$  for 24 h with shaking. After the polymerization, the THF solution was added to methanol. The precipitation (PUI-PM11, Figure 5) was filtered off and dried under reduced pressure.

For comparison with PUI-PM11, a liquid crystalline homopolymethacrylate (HPM11) was synthesized by the addition polymerization of M11.

## 2.3 Measurements

Monomers and polymers were identified by FT-IR and  $^1\text{H}$  NMR measurements. Molecular weights of polymers (PUI, PUI-PM11, HPM11) were determined by a Shimadzu GPC system (LC20AD-RID10A-GTO20A) in THF, calibrated against polysty-

rene standards. Phase transition behavior was measured with a Mettler-Toledo DSC1 and a Nikon ECLIPSE LV100POL microscope equipped with Mettler FP82 hot stage-Mettler FP90 temperature controller system. The DSC measurements were performed using an aluminum crucible containing about 10 mg of sample at a scanning rate of 10 °C/min.

### 3. Results and discussion

#### 3.1 Synthesis

Molecular weights of PUI, PUI-PM11, and HPM11 are summarized in Table 1.

Table 1: Molecular weights of polymers

Sample	$M_n$	$M_w$	$M_w/M_n$
PUI	37500	80900	2.16
PUI-PM11	38400	82500	2.15
HPM11	19000	42500	2.24

PUI-PM11 is a multiblock consisting of PU polymer (PUp) and PM11 units. PUI has a moderate distribution of AI units in the polymer chain, and AI unit is introduced for every ten units of PUp ( $M_n \approx 5300$ ) on average. The decomposition of AI generates PUp radicals. It has been reported that a multiblock is formed by the stopping reaction during the addition polymerization using a polyurethane polymerization initiator (Kinoshita et al., 1993). Consequently, PUI-PM11 is considered to be a multiblock consisting of alternately linked PUs and PM11 ( $M_n \approx 3400$ ) units, as shown in Figure 5.

#### 3.2 Phase transitions

Phase transitions of PUI, PUI-PM11, and HPM11 are summarized in Figure 6 and Table 2. PUI, with the azo radical initiator group, formed a nematic phase from glass-nematic ( $T_g$ ) to nematic-isotropic ( $T_{ni}$ ) phase transition temperatures on heating and cooling processes. PUI-PM11 also showed  $T_g$  and  $T_{ni}$ . HPM11 formed a smectic A phase from  $T_g$  to a smectic-isotropic phase transition temperature ( $T_{si}$ ). PUI cannot be mixed with HPM11, and a microphase separation was observed. However, PUI-PM11 formed only the nematic phase on the heating and cooling processes. A liquid crystalline polyurethane with the same repeating units as PUp also exhibits a nematic phase (Onouchi et al., 1996; Ujiie et al., 2022). Therefore, PUp and PM11 units exhibit different liquid crystalline phases from each other. These results indicate that PUp and PM11 units in PUI-PM11 are miscible with each other, forming a uniform nematic phase.

### 4. Conclusion

The liquid crystalline block copolymer consisting of liquid crystalline polyurethane and polymethacrylate units was synthesized using a polyurethane initiator. The polyurethane

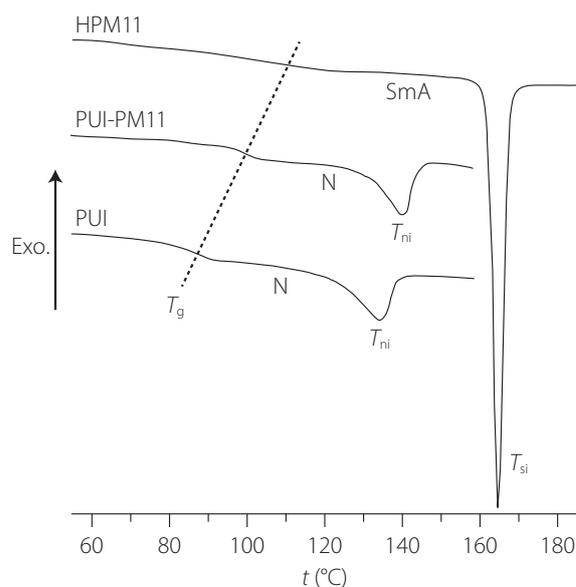


Figure 6: DSC curves of PUI, PUI-PM11, and HPM11

Notes:  $T_g$  = glass transition temperature,  $T_{si}$  = smectic A-isotropic phase transition temperature,  $T_{ni}$  = nematic-isotropic phase transition temperature. The point where the dashed line intersects the DSC curve is the glass transition temperature.

Table 2: Phase transitions of polymers <sup>(1)</sup>

Sample	$T_g / ^\circ\text{C}$	$T_{si} / ^\circ\text{C}$	$T_{ni} / ^\circ\text{C}$
PUI	91.6	–	134.4
PUI-PM11	98.1	–	140.1
HPM11	100.9	164.7	–

Note: (1)  $T_g$ ,  $T_{si}$ ,  $T_{ni}$ ; see Figure 6.

initiator and methacrylate homopolymer formed different mesophases of nematic and smectic phases, respectively. However, the liquid crystalline block copolymer, consisting of the corresponding polyurethane and polymethacrylate units, exhibited only the nematic phase on the heating and cooling processes. The nematic polyurethane initiator cannot be mixed with the smectic methacrylate homopolymer. However, the block copolymerization of two immiscible polymer units formed a liquid crystalline state in which these polymer units were uniformly miscible. This result indicates that block copolymerization is effective in the complexation of immiscible polymers. Furthermore, since the liquid crystalline block copolymer is an amphiphilic polymer composed of hydrophobic polyurethane and hydrophilic polymethacrylate, it is expected to be used as a polymer surfactant.

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