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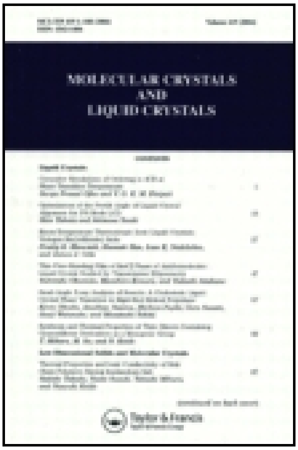

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Glass Forming Nematic Twin Molecules Synthesis and Polymerization Kinetics

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In this paper we describe the synthesis of a nematic twin molecule with a lateral methyl substituent in the mesogenic group. This compound exhibits a broad nematic mesophase between −18°C and 135°C and can be supercooled into a liquid crystalline glass. The LC-phase was permanently fixed into a network by in-situ photopolymerization. The broad mesophase of the twin molecule allows the investigation of the photopolymerization behaviour by photo-DSC-measurements in a wide tem-perature range. The T_g of the polymer network was determined by TMA-measurements.

Keywords: twin molecules; LC-glasses; photopolymerization kinetics; cholesteric networks

INTRODUCTION

More than 70 years ago, the first liquid crystalline twin molecules were described by Vorländer [1]. They were made from aliphatic bis-benzoic

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acids, which were esterified on both sides with azo mesogens. But only in the last years growing attention has been paid to twin molecules because they are good models for liquid crystalline main chain [2 - 4] and side chain polymers [5, 6]. Twin molecules have molecular weights in the range of oligomers, but are molecularly uniform. That makes them particularly attractive because they combine typical properties of polymers (glass formation) with those of low molar mass compounds, such as effective purification methods, well defined properties and an easy orientation of the mesophase compared to polymers. Nevertheless, in order to suppress crystallization in twin molecules a certain molecular geometry is necessary, e.g. the lateral connection of two mesogens by a flexible spacer [7, 8].

Low molecular mass glass forming nematics are very interesting for technical applications. Nematic monomers are often used as host in cholesteric mixtures, which are readily obtained by adding a chiral compound. If both the nematic and the chiral monomer contain polymerizable groups, the LC-phase can be permanently fixed in a network by in-situ photopolymerization of the oriented monomers. Further processing of the polymerized films leads to cholesteric pigments with a fascinating colour flop.

The production of the pigments, however, is not straightforward and costly. In contrast to common monomers which crystallize upon cooling, the use of mixtures which form LC-glasses allows solvent casting of the monomers even on large substrates. Such films can be stored for a certain time before photopolymerization.

In this paper, we describe the synthesis of the twin molecule Twin-2MHB with a broad nematic mesophase between -18°C and 135°C and glass forming properties. FIGURE 1 shows a schematical drawing of a twin molecule and the structure of Twin-2MHB.

The broad mesophase and the glass forming properties allow kinetic investigations over a wide temperature range. We investigated the polymerization kinetics by photo-DSC-measurements. TMA-measurements

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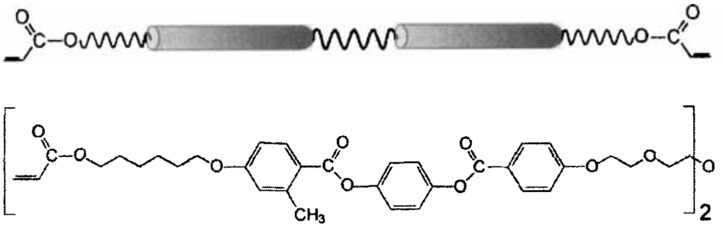
were used to determine the glass transition temperature (T_g) of the polymer network.



g -18 n 135 i

FIGURE 1 Schematic representation of a twin molecule and Twin-2MHB as example

EXPERIMENTAL

The photo-DSC-measurements were carried out using a Perkin Elmer DSC 7 with a Philips fluorescence lamp PL10 ($\lambda = 365$ nm; intensity 7 mW/cm^2, reduced with a grey filter to 0.7 mW/cm^2). The samples were prepared by adding 1 wt-% 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651, Ciba Geigy) as photoinitiator to the twin molecule. The mixture was dissolved in chloroform and the solvent allowed to evaporate. About 1 or 2 mg of this mixture were filled in a DSC-pan, purged for 3 minutes with nitrogen and irradiated with UV-light.

For the TMA-measurements samples of about 0.6 mm thickness were polymerized in their LC-phase at 100°C under nitrogen. The measurements were carried out in a Perkin Elmer TMA 7 with a heating and cooling rate of 5 K/min and a static force of 10 mN.

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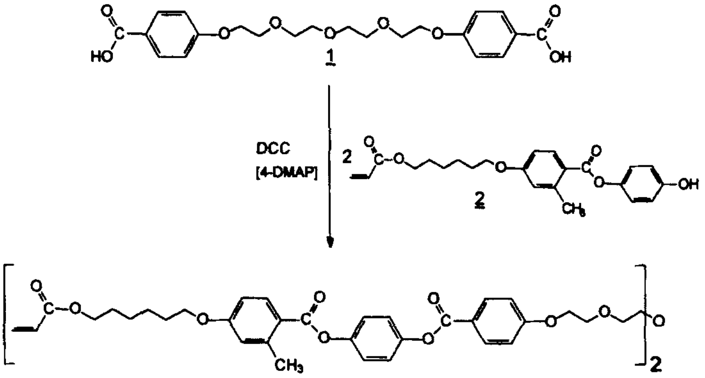
RESULTS AND DISCUSSION

Monomer synthesis and thermal behavior

The chemical structure of Twin-2MHB and the synthetic steps are shown in SCHEME 1. Both carboxylic groups of the tetraethylene glycol bis-benzoic acid 1 are esterified with the phenole derivative 2. The synthesis is described in more details in the literature [9, 10].

By polarizing microscopy and DSC-measurements the mesophase behaviour of Twin-2MHB was investigated. Only the first DSC-heating run shows a melting point at 54°C. This is due to the fact that during the workup the twin molecule is able to crystallize from solution. In the second and third heating and cooling runs only a glass transition at -18°C and the clearing point at 135°C are detected. In this temperature range a nematic mesophase is observed in the polarizing microscope. Crystallization is strongly suppressed in the monomeric state and starts after approximately three hours of annealing at room temperature.



SCHEME 1 Synthesis of Twin-2MHB

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Kinetic investigations of the in-situ photopolymerization by photo-DSC-measurements

In-situ photopolymerization of functionalized monomers is well established as a method for the preparation of liquid crystalline networks [11, 12]. The monomers are heated into the mesophase, oriented and irradiated with UV-light for a short time. This method has many advantages compared to a thermally initiated polymerization and to the use of LC-polymers. The low viscosity of the monomer mixture allows a good orientation of the mesogens. This orientation is preserved during photocrosslinking because of the high polymerization rate. The networks are stable up to their thermal decomposition. Moreover, the polymerization temperature can be chosen within the whole mesophase range.

The polymerization behaviour of acrylate monomers can be easily monitored by photo-DSC-measurements. The broad nematic range of Twin-2MHB allowed us to carry out the photo-DSC-measurements between 0°C and 140°C. In FIGURE 2 the time-conversion plot for Twin-2MHB at different polymerization temperatures is shown and in FIGURE 3 the final conversion vs. the polymerization temperature. The final conversion C_f [%] of the acrylate groups was detected from the heat of polymerization ΔH_{poly} [J g^{-1}] (integration of the DSC-curve) using the following equation

$$C_f = \frac{\Delta H_{poly} \, M}{2 \, \Delta H_{Ac}} \cdot 0.01$$

where M is the molecular weight of the monomer [g mol^{-1}] and ΔH_{Ac} the molar enthalpy of polymerization per acrylate group (78.000 J mol^{-1}) [13].

As known from literature [14], the final conversion strongly depends on the polymerization temperature. In our case densely crosslinked networks with a conversion of acrylate groups of more than 90% are obtained at polymerization temperatures higher than 80°C. At 0°C only a very low conversion of about 3% is observed, because the acrylate groups do not have enough mobility to react at this temperature any more. With increasing polymerization temperature the final conversion also increases. At 20°C we found a conversion of 39%, at 30°C even of 55%.

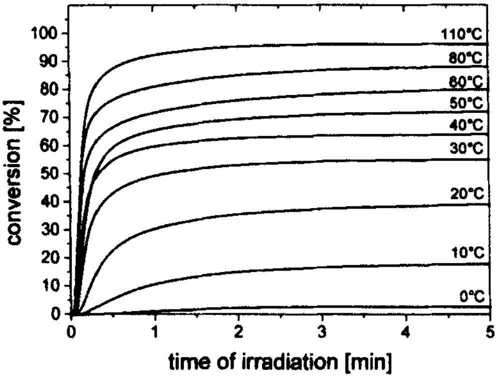

FIGURE 2 Time-conversion plot for Twin-2MHB at indicated polymerization temperatures

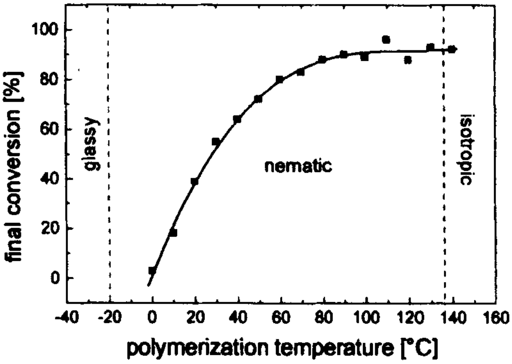

FIGURE 3 Final conversion vs. polymerization temperature for Twin-2MHB

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FIGURE 4 shows the polymerization rate R_{poly} as a function of the conversion for different polymerization temperatures (T_{poly} = 40°C, 60°C, 80°C, 110°C). R_{poly} is a normalized function, because the heat flow ΔQ_{poly} [J s^{-1}] depends on the weight of the sample [15, 16]. Therefore the absolute polymerization rate is divided by the initial monomer concentration

$$R_{poly} = \frac{\Delta Q_{poly}\, M}{m\, 2\, \Delta H_{Ac}} \left[s^{-1}\right]$$

where M is the molecular weight of the twin molecule [g mol^{-1}], m the mass of the monomer sample [g] and ΔH_{Ac} the molar enthalpy of polymerization per acrylate group (78.000 J mol^{-1}) [13].

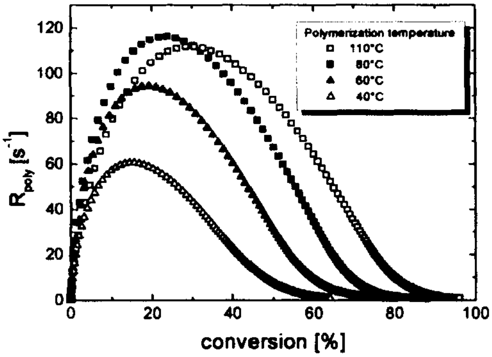

FIGURE 4 Polymerization rate vs. conversion for Twin-2MHB

First, all curves show an increase of R_{poly} to a maximum value. The maximum polymerization rates are already reached at low conversions, e.g. 15% at a polymerization temperature of 40°C and 31% at 110°C. At higher conversions the polymerization rate decreases to zero. This can be explained by an increase of the viscosity during network formation probably due to an increase in T_g, which strongly reduces the

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mobility of the remaining acrylate groups. Hence, no quantitative conversion of the acrylates can be achieved. For that reason the final conversion increases from 64% at a polymerization temperature of 40°C to 96% at 110°C. At higher temperatures, the increasing difference to T_g makes the acrylate groups more mobile at higher conversion. This explains the shift of the maxima of R_{poly} to higher conversions with increasing polymerization temperature.

Glass transition temperature of the polymer networks

Thermal Mechanical Analysis (TMA) is one method to determine glass transition temperatures of densely crosslinked networks [17]. As shown in FIGURE 5, the TMA-curve exhibits a linear behaviour below and above the glass transition temperature. At T_g the slope of the curve changes, what is typical for such a 2nd order transition. From the intersection point of the two slopes a T_g of 44°C was determined.

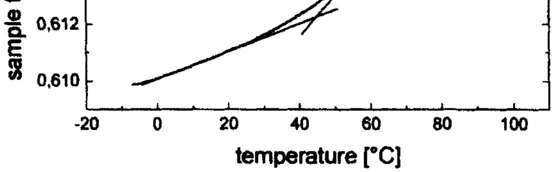

FIGURE 5 TMA-measurements of a network from Twin-2MHB (T_{poly} = 100°C)

That means that the T_g increases during the crosslinking process by about 60°C. This will also be shown for other twin molecules [9]. If the polymerization temperature approaches the T_g of the network, the monomers are frozen-in the glassy state and can not react any more.

CONCLUSION

The synthesis of the twin molecule Twin-2MHB is described in this paper. The lateral methyl group in the mesogenic core leads to a material with a broad nematic mesophase and which forms a LC-glass upon cooling. This behaviour allowed kinetic investigations of the photopolymerization over a broad temperature range. Thereby, we found final conversions of more than 90% at polymerization temperatures higher than 80°C. Below 80°C the final conversion decreases with decreasing polymerization temperature. During photopolymerization the glass transition increases from -18°C in the monomer to 44°C in a densely crosslinked network. The decrease of the final conversion of acrylate groups with decreasing polymerization temperature can thus be explained by a strong increase of the viscosity which lowers the mobility of the acrylate groups.

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