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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photopolymerization and Transport Properties of Liquid Crystalline Triphenylenes

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Version of record first published: 04 Oct 2006

To cite this article: I. Bleyl, C. Erdelen, K.-H. Etzbach, W. Paulus, H.-W. Schmidt, K. Siemensmeyer & D. Haarer (1997): Photopolymerization and Transport Properties of Liquid Crystalline Triphenylenes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 299:1, 149-155

To link to this article: http://dx.doi.org/10.1080/10587259708041987

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Mol. Cryst. Liq. Cryst., 1997, Vol. 299, pp. 149–155
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PHOTOPOLYMERIZATION AND TRANSPORT PROPERTIES OF LIQUID CRYSTALLINE TRIPHENYLENES

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Abstract The synthesis of polymerizable triphenylene derivatives with acrylate groups is described. The thermal properties and the photoconductive properties of the discotic monomers as well as of the polymers is investigated. In the mesophase typically photoinduced hole conductivity with a charge carrier mobility exceeding a value of 10^{-4} cm^2/Vs is observed with conventional time-of-flight (TOF) techniques. Different conditions for the photopolymerization of the acrylates in the mesophase are compared. The influence of the photoinitiators and the polymerization on the mesomorphic behavior and on the hole conductivity is described. Already the presence of small amounts of photoinitiator influences the packing within the mesophase. The polymerization further decreases the order and creates defects. This results in an at least one order of magnitude reduced charge carrier mobility at room temperature, compared to the monomer.

INTRODUCTION

Liquid crystalline alkoxy-substituted triphenylenes exhibit hole transport photoconduction in a discotic phase with charge carrier mobilities μ of about 10^{-3} cm^2/Vs[1,2]. In higher ordered phases the mobility is even increased by two decades[3]. This high photoconductivity makes triphenylenes promising candidates for technical applications, specifically as organic charge transport layers (CTL), in xerographic and opto-electronic applications. To achieve the required mechanical stabilities of the photoconducting layer, it is necessary to stabilize the mesophase in a polymer or a polymer network, while preserving order and charge mobility at room temperature. Recent investigations have shown that it is possible to polymerize substituted triphenylenes in thin films and orient the columns parallel to the surface[4]. The alignment of the discotic columns perpendicular to a surface that is necessary for fast photoconductivity has been up to now of unsatisfactory quality.

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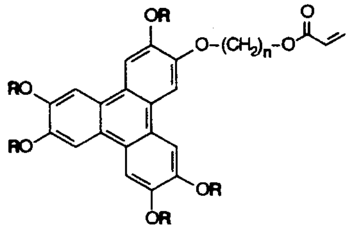
RESULTS AND DISCUSSION

Synthesis of the triphenylene monomers

The highly symmetric 2,3,6,7,10,11-hexaalkyloxytriphenylenes represent one of the most studied classes of discotic liquid crystals. They can be prepared by a convenient synthesis via trimerization of o-dialkyloxybenzenes[5]. During recent years the interest has been focused on functionalized and unsymmetrically substituted derivatives. These derivatives are accessible by either selective ether cleavage of symmetrical hexaalkyloxytriphenylenes[6], or by building the core stepwise from aromatic precursors. The latter so called 'biphenyl route', developed by Boden[5] and Ringsdorf[7] allows the systematic synthesis of unsymmetric triphenylene derivatives. According to the 'biphenyl route' several new hexaalkyloxytriphenylenes with an acrylate group (*1*-*5*) were synthesized.



No.	*1*	*2*	*3*	*4*	*5*
R	$-C_4H_9$		$-C_5H_{11}$		
n	2	3	2	4	6

All monoacrylates synthesized exhibit discotic liquid crystalline phases. In case of *1* a D_{ho}-phase is additionally confirmed by x-ray diffraction[8]. For all other cases the phases are assigned by polarization microscopy. The mesomorphic behavior of the acrylates is summarized in Table 1. The mesophase of all compounds supercools by at least 25 °C as observed by DSC (cooling rate: 10 K/min).

TABLE 1 Structures and transition temperatures (DSC, heating rate: 10 K/min) of the investigated triphenylene acrylates *1* - *5*

No.	k	T (ΔH) [°C] ([J/g])	k'	T (ΔH) [°C] ([J/g])	$p_?$	T (ΔH) [°C] ([J/g])	D_h	T_c*.(ΔH) [°C] ([J/g])	i
1	○	64 (39.3)					○	116 (8.7)	○
2	○	63 (7.3)	○	83 (23.8)	○	89 (11.3)	○	102 (8.4)	○
3	○	65 **			○	68 (54.3)	○	97 (6.8)	○
4	○	44 (38.3)					○	84 (5.2)	○
5	○	46 (43.8)					○	54 (4.3)	○

* T_c = clearing temperature, $p_?$ = uncharacterized phase

** ΔH is included in the following transition, because the peaks are not clearly separated

An increase of the length of the alkyl side-chains as well as of the spacer group between the aromatic core and the acrylate (from *1* to *5*) leads as expected to a reduction of the clearing temperature T_c and the corresponding transition enthalpy ΔH.

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Bulk polymerization in thin films

The polymerization reactions in about 10 μm thick films prepared by a doctor blade casting technique on microscopy slides were started in the mesophase either after purging with nitrogen or in vacuum after purging with nitrogen. Although the influence of the kind of photoinitiator or of the polymerization temperature on the rate of conversion is rather low, the product composition depends drastically upon whether the polymerization is carried out in a nitrogen atmosphere or in vacuum. The product composition is determined with an oligomer-GPC after dissolving the film from the microscopy slide with benzene and subsequent freeze drying. The influence of the polymerization conditions on the composition of the resulting films is summarized in Table 2.

TABLE 2 Influence of the photopolymerization conditions on the composition of the resulting films of various triphenylene monoacrylates. Composition determined by GPC analysis

	nitrogen purge						purge & vacuum				
initiator	Irgacure 651 1 mol %		Lucirin TPO 1 mol %				Lucirin TPO 3 mol %				
irradiation time [min]	5	5	5	15	5	15	10	10	10	10	10
temperature [°C]	90	110	90	90	110	110	95	84	79	66	41
compound	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*2*	*3*	*4*	*5*
monomer [%]	89	82	93	90	81	82	48	45	48	29	45
dimer [%]	9	13	6	8	12	11	1	<1	<1	1	1
mw > 10000 [%]	<1	<1	<1	<1	<1	<1	51	54	51	70	54

Table 2 demonstrates that for high conversion of the monomer, it is essential to rigorously exclude oxygen. Conversion rates higher than 50 % are only observed for the samples that were exposed to a nitrogen atmosphere and subsequently to vacuum for at least three times. It should be pointed out that a rate of conversion higher than 50 % is observed independent of the length of the side-chains and especially independent of the length of the spacer between the aromatic core and the polymerizable unit. Detailed studies on the polymerization of monomer *1* reveal that neither the nature of the initiator, nor the variation of the irradiation time or the polymerization temperature will result in the formation of polymer, if oxygen is not excluded from the monomer film by means of vacuum.

TOF experiments with monomers *1-5*

In a TOF experiment a sample with a typical thickness of 20 μm is sandwiched between two aluminum-covered glass electrodes. Electron-hole pairs are generated by irradiation of a strongly absorbed laser pulse (excimer laser: 20 ns; 308 nm) through one of the semitransparent electrodes. The field driven displacement of one kind of charge carriers is measured by transient currents, which can be recorded from 10^{-7} s up to 1 s. Details of the sample preparation and of the experimental setup are described in the literature[9].

The influence of the length of the side-chains, as well as of the spacer, in the polymerizable triphenylene derivatives on the charge carrier mobility is investigated with the neat compounds (without initiator). Since the different acrylates exhibit different transition temperatures, e.g. the clearing temperature T_c varies over a range of 60 °C, the TOF experiments are performed at a constant reduced temperature $\Theta = T_{meas}/T_c$. Table 3 compares the charge carrier mobilities of the monomers *1-5* at $\Theta = 0.95$.

TABLE 3 Influence of the side-chains and the spacer of the triphenylene-acrylates *1-5* on the charge carrier mobility in the mesophase at a reduced temperature $\Theta = T_{meas}/T_c \approx 0.95$ and an electric field of 20 kV/cm

Compound	*1*	*2*	*3*	*4*	*5*
μ [10^{-4} cm^2/Vs]	15	6	3	2	0.5
T_{meas} [°C]	93	80	80	60	40

The experimentally determined mobilities in the mesophases of the acrylate functionalized triphenylenes *1-5* differ by a factor of up to 30. Monomer *1* with butyloxy-side-chains and an ethyl-spacer exhibits the highest charge carrier mobility in this series, as high as $1.5 \cdot 10^{-3}$ cm^2/Vs. In general the charge carrier mobility of the monoacrylates decreases with an increasing length of the spacer between the aromatic core and the acrylate unit. However, there is also an influence of the side-chains too. The butyloxy-derivatives *1* and *2* show mobilities that are at least a factor of two higher, as compared to the pentyloxy-derivatives *3*, *4* and *5*.

Since T_{meas} varies over a range of 53 °C due to the different T_cs of the triphenylene derivatives *1-5*, thermal activation of the mobilities may influence the measured values at a given Θ of 0.95. Thermal activation energies can be determined from the temperature dependence of the zero-field-mobility $\mu_{E\rightarrow 0}$, by an extrapolation of the mobility $\mu(E)$ to $E = 0$. As a representative example, the field dependence of the charge carrier mobility of acrylate *2* is shown in Figure 1. For all investigated acrylates the field dependence is quite low or even not detectable. This is in good agreement with earlier measurements on liquid crystalline photoconductors based on triphenylenes[3,9].

An Arrhenius plot of the zero-field mobility leads to an activation energy E_{act} of about 200 meV for the charge carrier mobility. A plot of $\mu_{E\rightarrow 0}$ versus $1/T^2$ leads, according to the model of Bässler[10], to a value of $\sigma = 60$ meV for the width of the energy distribution of hopping sites. These low thermal activation energies cannot alter the trend

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visible in Table 2 for the mobilities in the investigated set of triphenylenes. Therefore the variations in the side-chains and spacer in the sequence from *5* to *1* lead to an increase in the charge carrier mobilities. Considering the thermal activation, the charge carrier mobility decreases by a factor two from *1* to *2*, i.e. substituting the ethyl-spacer by a propyl-spacer. Comparing the two derivatives with an ethyl-spacer (*1* and *3*) reveals that the substitution of the pentyloxy-side-chains with butyloxy-side-chains increases the mobility by a factor of four.

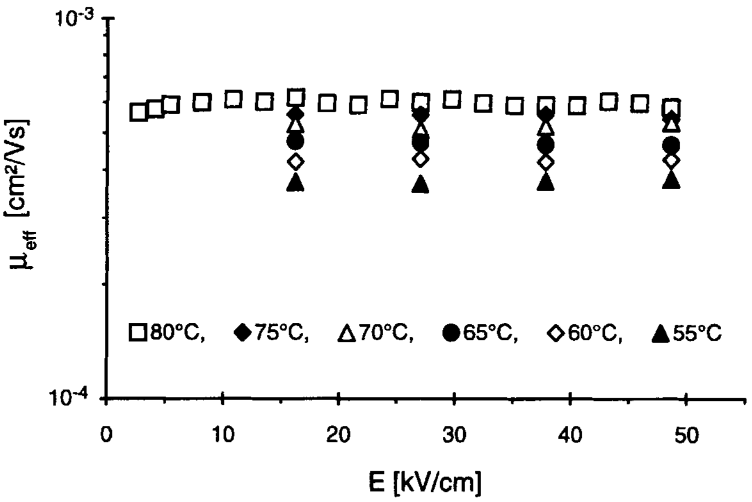

FIGURE 1 Field dependence of the charge carrier mobility at different temperatures as measured in monoacrylate *2* (tickness: d=17.5 μm)

The charge carrier mobility decreases in general with a broadening of the energy distribution of hopping sites and with an increasing intermolecular distance, which leads to a lower π-overlap along the columns[10]. On a molecular level the lower mobility can be explained with a less ordered packing of the discotic molecules within the columnar mesophase. This interpretation is supported by the decrease of the clearing temperatures, and corresponding enthalpies (Table 1), that are a measure for the stability of the mesophase structure.

Influence of polymerization on the charge carrier mobility

The photoinitiated polymerization reaction is carried out directly in the measuring cell, with almost simultaneous recording of the TOF currents. The influence of the polymerization on the photoconductivity is investigated in detail with monoacrylate *1* as well as *2* (Figure 2) as mixtures with 3 mol% Lucirin TPO and 500 ppm 2,6-Di-tert.-butyl-p-cresol as an inhibitor. To ensure good perpendicular alignment of the columns with respect to the electrodes of the measuring cell, the sample is first heated into the isotropic phase (T = 130 °C) and subsequently cooled down into the discotic phase (T_{meas} = 80 °C) at a rate of 1 K/min[3].

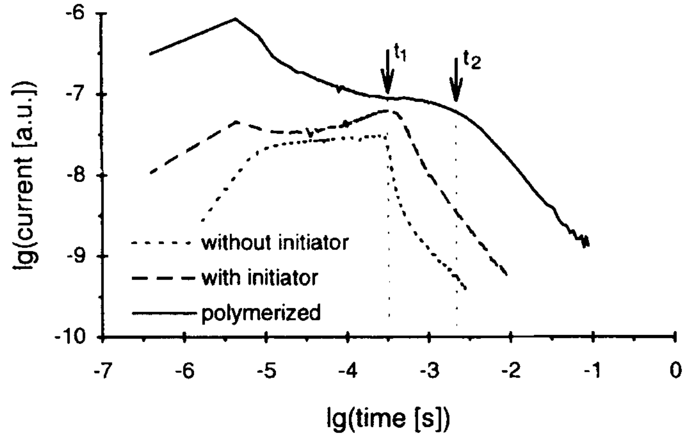

FIGURE 2 Current transients of monoacrylate *2* with 3 mol% LucirinTPO and 500 ppm 2,6-Di-tert.-butyl-p-cresol at 80 °C and 60 V, d = 19.5 μm. For a better visibility curves are shifted along the ordinate. Transit times t_1, t_2 are indicated by arrows

The comparison of the current transients with (— — —) and without (· · · ·) initiator show, that the initiator has little influence on the mobility. However, the sharpness of the current decay in the post-transit time regime decreases, indicating additional traps due to the initiator molecules. After photopolymerization at 80 °C the cell is measured again, showing drastically different current-transients (———). The first transit time is no longer detectable and instead a second transit time appears, representing mobilities of 10^{-4} cm²/Vs at 80 °C. The charge carrier mobility in the polymerized phase declines to $\mu = 10^{-5}$ cm²/Vs at room temperature.

CONCLUSION

All synthesized derivatives of triphenylene carrying an acrylate moiety as polymerizable group show a discotic-hexagonal phase. The clearing temperatures and corresponding enthalpies decrease with increasing length of the spacer groups. The charge carrier mobility of the monomers range from 1.5×10^{-3} to 5×10^{-5} cm²/Vs. The highest values for the hole mobility are measured for 2-(acryloyloxyethyloxy)-3,6,7,10,11-pentabutyloxytriphenylene *1*. Increasing the spacer length as well as substituting the butyloxy-side-groups by pentyloxy-side-groups decreases the charge carrier mobility. The mobility is

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weakly thermally activated with an activation energy of about 200 meV and does not depend on the electric field in the experimentally accessable field range.

Thin films of all acrylate substituted triphenylenes photopolymerize in the mesophase with more than 50% conversion. Small amounts of photoinitiator or inhibitor do not influence the photoconducting properties. In contrast, the polymerization reaction itself reduces the charge carrier mobility profoundly.

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EXPERIMENTAL

Materials:

The materials used,except the triphenylene derivatives, are commercially available and used as received. A detailed experimental procedure for the synthesis of the triphenylenes will be published elsewhere.

Bulk Polymerization reactions are carried out in about 10 µm thick films prepared by a doctor blade technique using 10 wt.% solutions in THF at room temperature on microscopy slides. Homogeneous mixtures of the triphenylene derivatives with 1 mol% or 3 mol% initiator (Irgacure 651 Ciba Geigy, Lucirin TPO BASF) are achieved by mixing appropriate amounts of benzene solutions followed by freeze drying. Photochemically initiated polymerization reactions are carried out on a precision hot stage (Gestigkeit PZ 28-2) in a nitrogen flushed box. The films are kept 5 min in the isotropic phase and cooled (1 °C/min) to the desired temperature, followed by irradiation (Amko LPS 210; Xe150W; 350 nm cut-off filter; neutral filter-25 % transmission) for 5 min and 15 min, respectively.
Alternatively the box was replaced by a desiccator cover (optical density ($\lambda > 320$ nm) < 1) placed directly on top of the hot plate. Oxygen was removed by evacuation and flushing with nitrogen. This procedure was repeated three times, before the sample was cooled to the polymerization temperature. The polymerization was carried out by irradiation for 10 min in vacuum as described above, but without the optical filters. The material is recovered by washing the slides with benzene followed by freeze drying.

TOF-experiments with pure materials or mixtures prepared as described for the bulk polymerization were performed with a sample preparation and a setup published already[9]. Polymerization reactions are performed in the measuring cell by irradiating through the semitransparent Al-electrodes.

Molecular weight determination is carried out with a Waters GPC (2 columns 8x600 mm; 50 nm, 5 mm and 10 nm, 5 mm) using THF as eluent with a flow rate of 0.5 ml/min

DSC-measurements were carried out on a Perkin-Elmer DSC 7.

Acknowledgement

S. Diele, Inst. für Physikalische Chemie, Universität Halle for the X-ray diffraction measurements. This work was supported by the BMBF-Project No. 03 M 4084 A0

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