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Thermal and Ferroelectric Stability of Liquid Crystalline Methacrylate Networks

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A series of ferroelectric liquid crystalline methacrylate networks was synthesized via bulk copolymerization. Electro-optical investigations revealed ferroelectric behavior (spontaneous polarization (P_S), ferroelectric switching, tilt angles) up to a certain degree of crosslinking. In this contribution we present a study of the ferroelectric properties with regard to their long term stability.

A considerable part of this work is focussed on the determination of the network structure, the degree of conversion and on the often unanswered question of the amount of monomer still present in the network, which cannot be extracted. We found that the crosslinking reaction reaches almost quantitative degrees of conversions. This was confirmed by infrared spectroscopy.

Keywords: ferroelectric networks; methacrylate polymers; thermal stability

INTRODUCTION

In an earlier publication, it was shown that it is possible to synthesize ferroelectric methacrylate networks in a one step copolymerization of monomers and crosslinking agent. These networks display ferroelectric properties which are significantly influenced by the amount of crosslinker used^[1]. However, the amount of unreacted monomer in the networks could not be determined by NMR and gravimetric methods only. Infrared spectroscopy

proved to be a valuable tool, to acquire information about the double bond conversion.

An important technological question is the long term stability of the materials. For possible applications, short switching times have to be realized. But even more important is the time, the networks can be used. Exemplary, the development of the ferroelectric properties over a period of time of more than 800 h was studied. To confirm these investigations, thermogravimetical studies were performed, based on publications, dealing with the well known problem of thermal degradation of methacrylic polymers ^[2,3].

MATERIALS

Figure 1 shows the monomers used to assemble the networks. The synthesis of the S_C -monomer **1** 4-(1-methylheptyloxy)-4'-biphenyl-4-[ω -(2-methylpropenoyloxy)undecyloxy]benzoate^[4], the crosslinking agent **2** 1,4-phenylene bis[$\{\omega$ -(4-methacryloyloxy)hexyloxy]benzoate^[5] and the polymers and networks are described elsewhere^[1]. As photo-initiator α,α -Dimethoxy- α -phenyl-acetophenon (Fluka) was employed. In the following, the homopolymer of **1** is depicted as **P11**, the networks as **N02 – N2**, where **N02** means 0.2 mol% crosslinking agent. All long term experiments shown here were performed with **N02** networks.

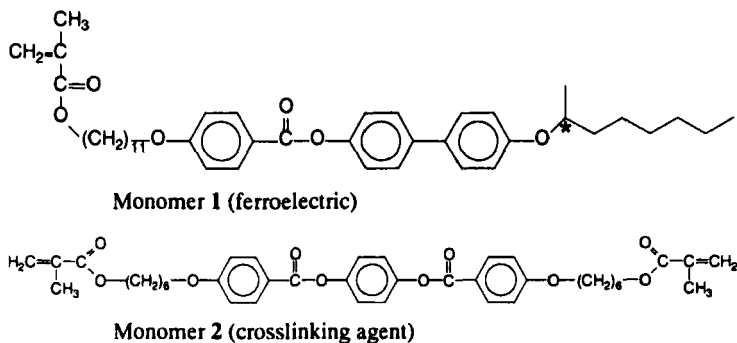


FIGURE 1 Monomers

ELECTROOPTICAL INVESTIGATIONS

In order to examine the long term behavior of the ferroelectric properties, the networks were heated up to 140°C into their $S_{C^{**}}$ -phase. The lc behavior is summarized in table 1.

TABLE 1 DSC data (rate 10 K/min, 2nd DSC heating traces) of the linear homopolymer **P1** and networks **N01** to **N2** (S_X : not properly identified, probably S_F)

Sample	T _g (°C)	T (S_X - $S_{C^{**}}$) (°C)	$\Delta H(S_X$ - $S_{C^{**}})$ (J/g)	T ($S_{C^{**}}$ -i) (°C)	$\Delta H(S_{C^{**}}$ -i) (J/g)
P1	69	137	2.28	152	8.57
N01	65	134	1.71	150	8.64
N02	60	134	2.03	152	7.46
N03	58	133	1.57	150	8.08
N04	59	133	1.02	152	7.77
N05	67	132	1.11	150	8.91
N1	63	131	0.02	153	7.63
N2	62	-	-	154	7.05

Long-term measurements were performed on samples **N02**. A rectangular voltage of ± 50 V/4 μ m, 1 Hz was applied and the EHC-cell (supplied by E.H.C. Co., Ltd., Japan) was left to switch for over 60 h. Then the network was cooled down to room temperature and set aside for 48 h. It was heated up to 140°C again and switched with an applied voltage. This was done, until one cell was successively switched for over 800 h, which means that the mesogens changed their orientational state over $2.88 \cdot 10^6$ times. Figure 2 illustrates the optical switching time versus time of application.

Over the whole period of 800 h, the optical switching time remains constant at around 20 ms within the experimental error. It can be concluded, that long loads of temperature and/or voltage do not influence the ferroelectric switching and that the network structure will not be effected. This result is also

supported by the behavior of the optical tilt angle. While measuring the tilt angle in the course of the experiment, no remarkable changes were observed. It remains constant within the experimental error between 29° and 32° , depending on the temperature.

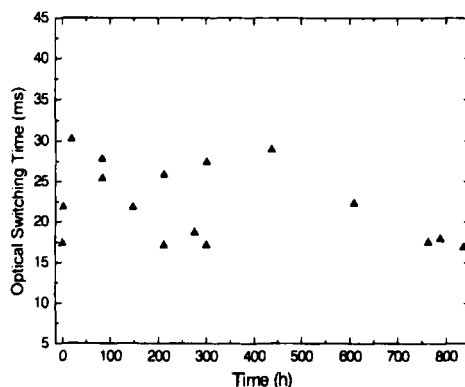


FIGURE 2 Time dependence of the optical switching time (switching realized with ± 50 V/ $4 \mu\text{m}$, 1 Hz) of a sample **N02**

The course of the spontaneous polarization on the other hand changes with the duration of the experiment, as can be seen in figure 3. Within 400 h P_3 drops from its initial value of 60 nC/cm^2 to a plateau value of approximately 40 nC/cm^2 , which is about the value of the monomer **1**-analogous hydrogenated substance with no double bond^[4]. However, a depolymerization can be excluded, since the isotropization temperature (T_i) of the material does not change. A newly synthesized network displays a T_i of 152°C , which is the same value obtained from a network, that has been switched for over 800 h. If the network would depolymerize or degrade, the isotropization temperature should decrease, since non-liquid crystalline areas would appear. This is not the case; but some reorganization processes have to take place, since P_3 decreases. A possible explanation might be further crosslinking, which causes

the network to become tighter and thus more rigid, without increasing the isotropization temperature (see table 1).

If and how the network structure changes in the course of the long term experiment cannot totally be examined, since it is impossible to remove the materials from the measuring cell, without destroying it.

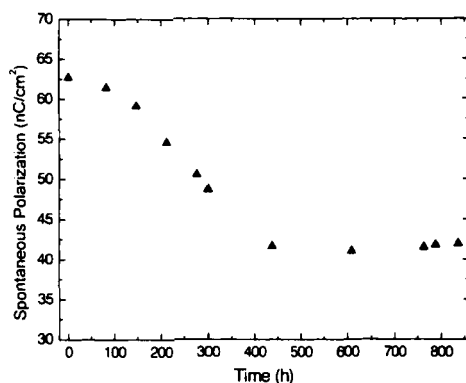


FIGURE 3 Time dependence of the spontaneous polarization (P_S measured with ± 50 V/4 μm , 0.5 Hz) of a sample **N02**

THERMOGRAVIMETRICAL INVESTIGATIONS

In order to investigate possible degradation processes, the networks were characterized by thermogravimetical analysis, using a PL-STA 1000 from Rheometric Scientific Ltd., Bensheim. The material (5–10 mg) was placed in an aluminum pan and heated up with 10 K/min to 600°C in an environment set up of air, in order to simulate rather harsh conditions. The obtained traces are shown in figure 4. As can be seen in figure 4, the higher the crosslinking density, the earlier the sample mass starts to decrease. In the liquid crystalline region (until 152°C), no weight loss is detected. Between 250°C and 300°C no weight loss was recorded for the uncrosslinked homopolymer, while network loose between 1 % to 3 % mass with increasing degree of crosslinking. Above

350°C all materials degrade. This can be explained by taking the molecular structure of the components into account.

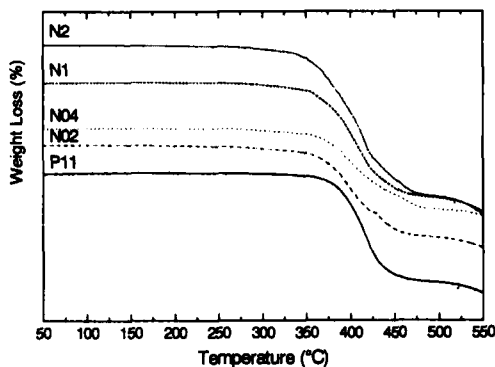


FIGURE 4 Thermogravimetric traces of various networks
(rate 10 K/min)

The crosslinking agent 2 has two carboxyl groups, which can decarboxylate in an oxidative environment, such as air. If these two groups degrade, the remaining fractions will be lighter than those remaining after the decarboxylation of monomer 1. It can be concluded from these investigations, that the networks can be employed at 140°C without major degradation in the EHC-cells.

IR-SPECTROSCOPY

As described in a previous publication, the degree of conversion was determined by NMR-investigations and swelling measurements^[1]. However, the gravimetric results obtained from the swelling-measurements are not as accurate as results obtained from spectroscopy. Liquid NMR-spectroscopy on

swollen lc networks delivers only a vague idea of the conversion, since not all groups can be resolved in the NMR-spectra, due to hindered rotation.

Therefore we employed infrared spectroscopy to determine the degree of double-bond conversion. IR spectra of monomer **1** and the corresponding hydrogenated substance were recorded to clearly identify the C=C-double bond signal, which shows resonance at 1640 cm^{-1} .

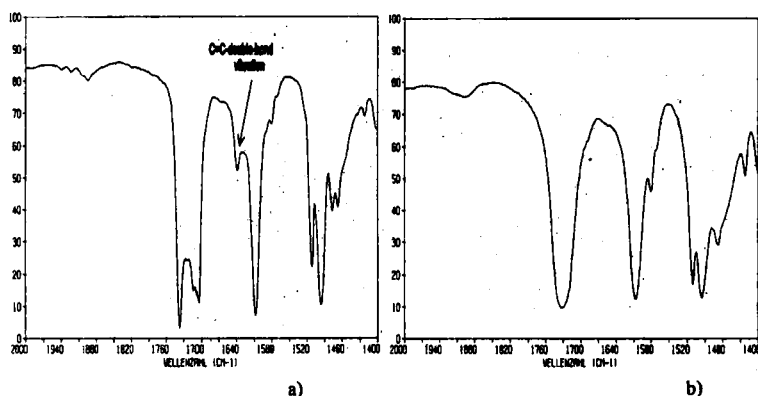


FIGURE 5 a) IR-transmission spectra of monomer **1**;
b) spectra of a network with 1 mol% **2**

In all spectra of the networks, no signal at 1640 cm^{-1} was detected. However, this signal is partially superposed by the C-C-bond vibration, which hinders the exact evaluation of the obtained results. Figure 5 shows IR-spectra of monomer **1** and of a network. From these spectra and the results obtained from NMR-spectroscopy and swelling experiments, it can be concluded that the crosslinking copolymerization of lc monomers and crosslinker leads to networks with high degrees of conversion, which does not contain non-extractable monomers. These results confirm other investigations concerning the crosslinking of lc monomer. Even lc-polymer-composites show a high degree of conversion, which is derived from the ordered arrangement of the mesogens prior to polymerization [6,7]. It was shown, that the yielded

conversion of photo-initiated polymerizations are always higher than those of non-lc monomers, respectively ^[8].

CONCLUSIONS

We have demonstrated, that methacrylic networks are capable of retaining their ferroelectric properties over long periods of time, without mayor changes in the polymer system (exception: the initial value of P_r drops to a plateau value). Additionally, we were able to confirm results obtained from NMR- and gravimetrical measurements concerning the determination of the degree of conversion. By IR-spectroscopy, high degrees of conversion were detected and no non-extractable monomers were found in the synthesized lc networks.

Acknowledgments

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