**Communication:** The ATRP (atom-transfer radical polymerization) process was used to synthesize  $C_{60}$  endcapped polystyrene. GPC data demonstrated that fullerene ( $C_{60}$ ) was chemically bonded to polystyrene, and  $C_{60}$  was most likely monosubstituted. Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry (MS) analysis (with 1,8-dihydroxy-9(10H)anthracenone (dithranol)/silver trifluoroacetate as the matrix) of this copolymer proved that  $C_{60}$  was monosubstituted.



# MALDI-TOF mass spectrometry characterization of $C_{60}$ end-capped polystyrene prepared by ATRP

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## Introduction

Polymeric  $C_{60}$  derivatives are highly intriguing in that they have extraordinary properties on conducting, magnetic, photochemical, electrical,<sup>[1,2]</sup> and microtribological<sup>[3]</sup> aspects. Various possibilities<sup>[2]</sup> have been reported on the synthesis of these derivatives during recent years. However, many of the derivatives are crosslinked and non-processable due to multisubstitution. In order to improve the processability, it is necessary to obtain the monosubstituted products. So far, reports on monosubstituted products are based on the reaction of functional polymers with C<sub>60</sub>, for example, azido-terminated polystyrene,<sup>[4]</sup> amino-terminated polystyrene,<sup>[5]</sup> and TEM-POL-terminated polystyrene (TEMPOL = 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy).<sup>[6]</sup>

With the introduction and development of atom-transfer radical polymerization (ATRP),<sup>[7]</sup> this simple and effective method has gained increasing interest. In this paper, we give an account of the synthesis of  $C_{60}$  end-capped polystyrene (PS- $C_{60}$ ) by ATRP. To determine the structure of the copolymer, we used MALDI-TOF MS, since it is a fast and simple technique for qualitative chain-end analyses. Recently, several groups reported on the characterization of polymers by means of MALDI MS.<sup>[8-10]</sup>

# **Experimental part**

#### Materials

Styrene and toluene were distilled before use. Copper(I) bromide (CuBr), fullerene ( $C_{60}$ , 99.9 wt.-%), 1-phenylethyl

bromide (1-PEBr), 2,2'-bipyridine (bpy) were used as received.

#### Synthesis of bromo-terminated polystyrene

The polymerization was carried out according to a procedure reported by Wang.<sup>[7]</sup> A reddish brown mixture of styrene, 1-PEBr, CuBr (1 molar equiv. relative to 1-PEBr), and bpy (1 molar equiv. relative to CuBr) was degassed in a glass tube by several freeze-thaw cycles under vacuum, then the tube was sealed off and immersed in an oil bath at 110 °C. After 8 h reaction time, the solution was very sticky. It was dissolved in trichloromethane (CHCl<sub>3</sub>) and filtered. Under stirring, the solution was added dropwise into an excess of methanol. The polymers were isolated by filtration, washed with methanol, and dried. The data of the polymerization were summarized in Tab. 1, and the general synthetic route is shown in Scheme 1.

Tab. 1. GPC analysis of polystyrene synthesized by ATRP.

Sample	Reaction time in h	$\overline{M}_{ m n}$	$\overline{M}_{ m w}$	$\overline{PD}$	Conversion in %
PS-I	20	2060	2980	1.45	64.9
PS-II	20	2550	3580	1.40	84.5

### Synthesis of $C_{60}$ end-capped polystyrene

The reaction was carried out by mixing bromo-terminated polystyrene, fullerene ( $C_{60}$ ), CuBr and bpy in a glass tube with toluene. An excess of  $C_{60}$  was used according to Weis.<sup>[5]</sup> In all reactions, a ratio of 1.5:1  $C_{60}$ /bromo-terminated polymer was used. The solution was degassed by freeze-thaw



Propagation:



Scheme 1.

Scheme 2.

Tab. 2. GPC analysis of C<sub>60</sub>-polystyrene synthesized by ATRP.

Sample	Reaction time in h	$\overline{M}_{ m n}$	$\overline{M}_{ m w}$	$\overline{PD}$
PS-C <sub>60</sub> (I)	20	2960	3 8 9 0	1.31
$PS-C_{60}(II)$	20	3340	4400	1.32
PS-II <sub>control</sub>	20	2340	3680	1.57

cycles under vacuum. The tube was sealed off and immersed in an oil bath at 110 °C for 12 h. A control sample using PS-II was prepared under the same conditions. After filtration, the solution was added dropwise into an excess of methanol under stirring. The resulting precipitate was dissolved in tetrahydrofuran (THF) to remove unreacted  $C_{60}$ , and THF was then removed by rotary evaporation. The so obtained crude polymer consists of a mixture of polystyrene and  $C_{60}$ -polystyrene. Thin layer chromatography (silica) was used to separate  $C_{60}$ -polystyrene from polystyrene; a mixture of toluene, tetrachloromethane and acetic acid (1:1:0.25) was used as the eluent.  $C_{60}$ -polystyrene was received as a brown powder with a yield of 35-37%. The data of the reaction are summarized in Tab. 2, and the general synthetic route is shown in Scheme 2.

## Gel permeation chromatography (GPC)

GPC was performed using a Waters apparatus working at 35 °C with stabilized tetrahydrofuran (THF) as the eluent at a flow rate of 1 ml  $\cdot$  min<sup>-1</sup>, equipped with three Styragel columns (HT2, HT3, HT4), and with polystyrene as standard. Differential refractive index detector and UV detector were used respectively.

## MALDI-TOF mass spectrometry

MALDI-TOF MS was performed using a Bruker time-offlight mass spectrometer. The instrument was equipped with nitrogen laser (337 nm), delayed extraction and reflector. It was operated at an accelerating potential of 20 kV in linear mode. The MALDI mass spectra represent averages over 100 consecutive laser shots (3 Hz repetition rate). The samples (10 mg/ml), dithranol matrices (20 mg/ml) and silver trifluoroacetate solution (10 mg/ml) were all prepared in THF. The ratio of the sample to matrice and silver trifluoroacetate is 10:10:1. A 2  $\mu$ l portion of the final solution was deposited onto the sample target and allowed to dry at room temperature and ambient atmosphere.

## **Results and discussion**

All samples were dissolved in THF giving golden brown solutions. According to Weis<sup>[5]</sup> and Wang,<sup>[6]</sup> we used the GPC equipped with a UV detector at 350 nm to demonstrate that C<sub>60</sub> and polystyrene are chemically bonded because polystyrene can be detected only at 254 nm, while PS-C<sub>60</sub> copolymer can be detected at wavelengths ranging from 300 to 350 nm. Fig. 1 shows the GPC results utilizing the UV detector. In contrast to the control sample from PS-II, it becomes clear that C<sub>60</sub> and polystyrene are chemically bonded. Comparing Tab. 1 and Tab. 2 reveals that the molecular weights of C<sub>60</sub> end-capped polystyrene [PS- $C_{60}(I,II)$ ] are just similar to their bromoterminated precursors [PS-I,II]: each one increased in about 1000 in molecular weight. This means that most likely one bromo-terminated polystyrene molecule



Fig. 1. GPC curves of  $PS-C_{60}(I,II)$  and control PS-II measured with a UV detector at 350 nm (A:  $PS-C_{60}(I)$ , B:  $PS-C_{60}(II)$ , C: control PS-II).

reacted with one  $C_{60}$  molecule resulting in monosubstituted  $C_{60}$ .

With respect to MALDI-TOF studies, it was reported by Charleux<sup>[8]</sup> that no polymer has a single, narrow molar mass distribution, although MALDI-TOF mass spectra should give results similar to those by means of GPC. In order to compare with C<sub>60</sub>-polystyrene, samples of mixtures of polystyrene [PS-(I,II)] and powdered C<sub>60</sub> were studied using MALDI-TOF. It is shown in Fig. 2 that C<sub>60</sub> can be obviously observed at m/z = 720, and we attributed two principle ion series of polystyrene which can be distinguished and assigned as:

$$\begin{bmatrix} \bigcirc -CH-(sty)_{\overline{n}} CH=CH-\bigcirc +Ag^{+} \end{bmatrix}$$
  
Series A



Interestingly, no polymer with bromo end group was detected. It may be probable that the covalent bromo-



Fig. 2. MALDI-TOF mass spectra obtained with dithranol/silver trifluoroacetate matrix for polystyrene samples PS-I,II mixed with  $C_{60}$ .

linkage was easily broken in the process of analysis. No bromo end group could be detected with the dithranol/silver trifluoroacetate matrix.

MALDI-TOF spectra of the C<sub>60</sub>-polystyrene samples presented in Tab. 2 are shown in Fig. 3. With the structure of series B and the existence of methyl group fragments in the high laser energy field, we tentatively attribute that the bromo-terminated polystyrene subsequently reacted with C<sub>60</sub> under rearrangement of  $-CH_3$  to the thermodynamically most stable isomer. The principle ion series of C<sub>60</sub>-polystyrene can be distinguished and assigned as:







Fig. 3. MALDI-TOF mass spectra obtained with dithranol/silver trifluoroacetate matrix for  $C_{60}$ -polystyrene samples PS- $C_{60}(I,II)$ .

One further series is evident but has not been assigned yet. Still the bromo end group can not be detected this way. But from the MALDI data, we can be sure that  $C_{60}$ was monosubstituted since the data are in agreement with each other. Tab. 3. shows the corresponding masses for the three series A, B and C.

Tab. 3. MALDI-TOF experimental molar masses of Ag<sup>+</sup>-ionized samples (dithranol/silver trifluoroacetate matrix).

Observed masses	Identified series	Samples including the series
1358, 1462, 1566	series A	PS-I, PS-II
1373, 1477, 1581	series B	PS-I, PS-II
2302, 2406, 2510	series C	PS-C <sub>60</sub> (I), PS-C <sub>60</sub> (II)

## Conclusion

 $C_{60}$  end-capped polystyrene was successfully synthesized by the ATRP method. MALDI-TOF mass spectrometry characterization of the samples with dithranol/silver trifluoroacetate as the matrix demonstrates that  $C_{60}$  was monosubstituted. However, the mechanism of the fragmentation needs further research.

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