Preparation and characterization of soluble pendant [60]fullerene-polystyrene polymers

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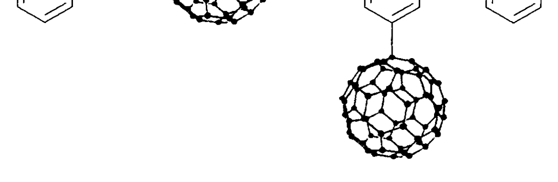
Pendant [60]fullerene-polystyrene polymers soluble in organic solvents are prepared by fullerenating polystyrenes in Friedel–Crafts type reactions, and characterized by using gel permeation chromatography, NMR, FTIR, thermal analysis and optical spectroscopic methods.

Recently, polymeric fullerene materials have received great attention.[1–4] Of particular interest are polystyrene-based fullerene polymers[5–11] because of their potential technological applications. It has been shown[5–7] that [60]- and [70]-fullerene can be incorporated into polystyrene structures by copolymerizing fullerene and styrene in free radical polymerization reactions. The known polystyrene-bound fullerene materials also include pendant [60]fullerene-poly(styrene-co-azidomethylstyrene) polymers[8] and so-called flagellenes.[9] Here we report the preparation of pendant [60]fullerene-polystyrene polymers† by use of Friedel–Crafts type reactions.[11] The pendant polymers are soluble in organic solvents such as chloroform, which allows characterizations using solution-based techniques. The fullerenation of polystyrene provides a facile method of homogeneously dispersing fullerene molecules into polymer matrices in a structurally somewhat controllable fashion.

In a typical experiment for the pendant polymer preparation, 29 mg of [60]fullerene ($>99.5\%$) and 104 mg of polystyrene were dissolved in 20 ml CS_2, forming a purple solution. The solution was mixed with *ca.* 10 mg of the catalyst anhydrous $AlCl_3$ in a vial, and then sealed. After 12 h of reaction at room temperature with stirring, the solution becomes dark brown.

The reaction was quenched by the addition of 10 ml water. After phase separation, the aqueous phase was removed and the remaining CS_2 fraction was washed with water to remove residual catalyst $AlCl_3$. Evaporation of the solvent CS_2 yielded black solids, which were mixtures of pendant [60]fullerene-polystyrene polymers and unreacted [60]fullerene. The solids were extracted with chloroform (5 ml × 2) to yield a reddish brown solution. The solid residue contained the bulk of the unreacted [60]fullerene because of its poor solubility in chloroform. A small amount of the unreacted [60]fullerene was still in the polymer solution. The pendant polymers were then precipitated from the chloroform solution by adding methanol (1 : 1). The precipitation procedure was repeated until the residual chloroform–methanol solution became colourless. The average [60]fullerene contents in the pendant polymers (Table 1) were estimated on the basis of the recovered unreacted [60]fullerene.



Two kinds of polystyrene samples were used. The polystyrene with a somewhat broad weight distribution was prepared by free radical polymerization of styrene using benzoyl peroxide as an initiator, while the linear polystyrene standards were obtained commercially. There seem to be no apparent differences for the two kinds of polystyrene samples in the reactions.

The solubilities of the pendant [60]fullerene-polystyrene polymers in organic solvents are strongly dependent on the sample history. Freshly prepared pendant polymers are soluble in chloroform. However, as the solvent is removed completely by using a rotary evaporator, the solid polymer sample thus obtained can not be re-dissolved in the same solvent, even with soaking for an extended period of time. Therefore, a complete removal of the solvent was avoided in the preparation of the pendant [60]fullerene-polystyrene polymers used in this study.

The pendant [60]fullerene-polystyrene polymers were characterized by GPC using linear polystyrene standards. The sample solutions were filtered through a 0.2 μm teflon filter before injections. Fig. 1 shows a comparison of GPC results of the pendant polymer and its corresponding parent polystyrene. The pendant polymer has a higher average molecular weight and a somewhat broader weight distribution (Table 1). For the pendant polymers from higher molecular weight polystyrenes, GPC results are somewhat more complicated. There are small peaks with elution times much shorter than that of the main peak in the GPC chromatogram. These small peaks may be attributed, at least partially, to the formation of polymer aggregates in the elution process. Further GPC characterizations in different solvents are required for a more definite conclusion.

^1H NMR spectra of the pendant [60]fullerene-polystyrene polymers are essentially the same as those of their corresponding parent polystyrenes. The results are understandable because the loading of [60]fullerene in the pendant polymers is relatively low and the mole fraction of the styrene units that are fullerenated is rather small (Table 1). However, in the ^{13}C NMR spectra of the pendant polymers (75.5 MHz, CCl_3D solution,

Table 1 GPC Results of parent polystyrenes and pendant [60]fullerene-polystyrene polymers

Polystyrene		Pendant Polymer		
M_w	Poly-dispersity	[60]Fullerene/ mass%	M_w	Polydispersity
16000[a]	1.8	*ca.* 10	43 000	3.6
6000[b]	1.11	*ca.* 8	10 100	1.4
24000[b]	1.03	*ca.* 8	26 300[c]	1.3[c]
132300[b]	1.03	*ca.* 10	470 000[c]	5.4[c]

[a] Obtained from free radical polymerization of styrene with benzoyl peroxide as an initiator. [b] Linear polystyrene standards obtained commercially from the Polymer Source, Inc. [c] Calculated by considering only the main peak in the GPC chromatogram.

ca. 30,000 scans), there is a weak and extremely broad peak in the δ 140–155 region in additional to the intense signal due to polystyrene. The extremely broad ^{13}C NMR signal in the so-called fullerene region is typical for polymer-bound [60]fullerene molecules.[6,7,12]

FTIR spectra of the pendant polymers are similar to those of the corresponding parent polystyrenes (Fig. 2). However, a visually different feature in the spectra of the pendant polymers is an absorption band at 527 cm^{-1}, which corresponds to the most intense band in the FTIR spectrum of [60]fullerene. This absorption band often survives in the functionalization of the [60]fullerene cage.

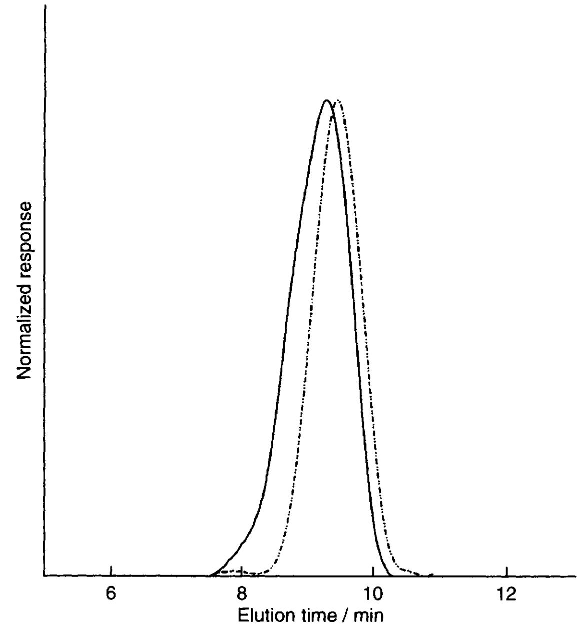


Fig. 1 A comparison of GPC chromatograms of the parent polystyrene (-..-..-; M_w 16 000, polydispersity 1.8) and the pendant [60]fullerene-polystyrene polymer (——; M_w 43 000, polydispersity 3.6)

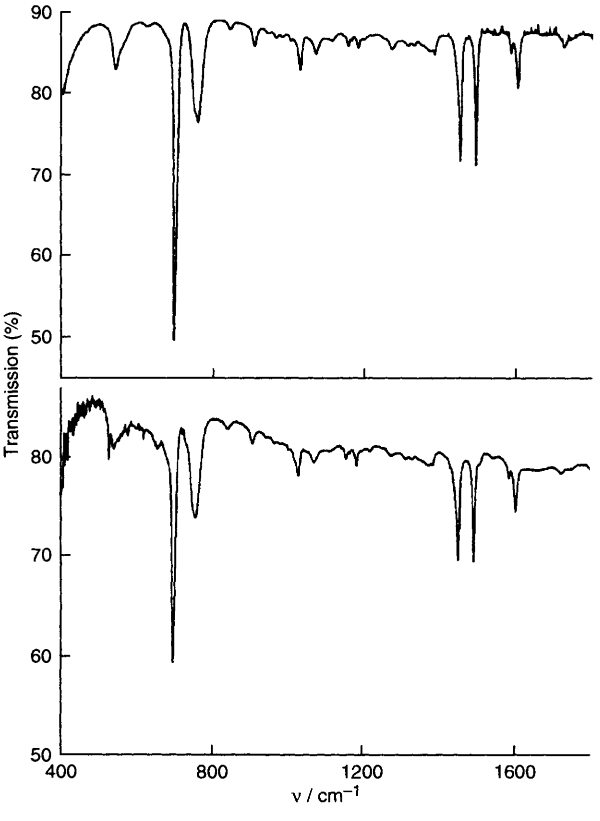


Fig. 2 FTIR spectra of polystyrene (top; M_w 16 000, polydispersity 1.8) and the corresponding pendant [60]fullerene-polystyrene polymer (bottom)

Differential scanning calorimetry (DSC) results of the pendant [60]fullerene-polystyrene polymers were compared with those of the corresponding parent polystyrenes. While the parent polystyrenes have well-defined glass transition temperatures, no glass transitions can be observed for the pendant polymers under the same experimental conditions. Apparently, the pendant [60]fullerene-polystyrene polymers reported here are thermochemically different from the pendant [60]fullerene-poly(styrene-co-azidomethylstyrene) polymers, for which an increase in glass transition temperature with increasing [60]fullerene loading was reported.[8] The lack of glass transition in the [60]fullerene-polystyrene polymers might be due to crosslinking,[13] which is possible as a result of multiple functionalization of a single [60]fullerene cage in the Friedel–Crafts type reactions. However, the GPC results seem to suggest only limited crosslinking† if it is assumed that the size-exclusion behaviour of the fullerenated polystyrenes is the same as that of linear polystyrene standards in GPC measurements.

The electronic absorption and emission spectra of the pendant [60]fullerene-styrene polymers are interesting. Absorption spectra of the pendant polymers in the visible region are very different from that of free [60]fullerene. The somewhat structured absorption band of free [60]fullerene is replaced by a steadily decreasing curve, typical for substituted [60]fullerene. In the UV region, the absorption band due to polystyrene moiety can still be observed. The fluorescence spectra of the pendant copolymers excited in the visible region are broad, with the peak maxima at *ca.* 650 nm. The spectra are also very different from that of free [60]fullerene. However, it is very interesting that the fluorescence spectra of the pendant [60]fullerene-polystyrene polymers are remarkably similar to those of the [60]fullerene-styrene copolymers obtained from free radical copolymerization reactions,[5–7] despite their expected structural differences.

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Footnote

† Although there are probably limited crosslinkings in the fullerenated polymers, the basic polymer structures may still be close to those of pendant polymers. In that context, the fullerenated polymers are referred to as pendant [60]fullerene-polystyrene polymers both for convenience and for the relationship to the true pendant polymers.

References

1 I. Amato, *Science*, 1991, **254**, 30.
2 J. E. Fischer, *Science*, 1994, **264**, 1548.
3 A. Hirsch, *Adv. Mater.*, 1993, **5**, 859.
4 K. E. Geckeler, *Trends Polym. Sci.*, 1994, **2**, 355.
5 T. Cao and S. E. Webber, *Macromolecules*, 1995, **28**, 3741.
6 C. E. Bunker, G. E. Lawson and Y.-P. Sun, *Macromolecules*, 1995, **28**, 3744.
7 A. G. Camp, A. Lary and W. T. Ford, *Macromolecules*, 1995, **28**, 7959.
8 C. J. Hawker, *Macromolecules*, 1994, **27**, 4836.
9 E. T. Samulski, J. M. DeSimone, M. O. Hunt Jr., Y. Z. Menceloglu, R. C. Jarnagin, G. A. York, K. B. Labat and H. Wang, *Chem. Mater.*, 1992, **4**, 1153.
10 C. Weis, C. Friedrich, R. Mülhaupt and H. Frey, *Macromolecules*, 1995, **28**, 403.
11 G. A. Olah, I. Bucsi, C. Lambert, R. Aniszfeld, N. J. Trivedi, D. K. Sensharma and G. K. S. Prakash, *J. Am. Chem. Soc.*, 1991, **113**, 9387.
12 B. Ma, G. E. Lawson, C. E. Bunker, A. Kitaygorodskiy and Y.-P. Sun, *Chem. Phys. Lett.*, 1995, **247**, 51.
13 A. Rubin, *The Elements of Polymer Science and Engineering*, Academic Press: New York, 1982.

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